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Liquid-Liquid Extraction of Trace Level Pesticides from Process Streams

S-Cubed, La Jolla, CA

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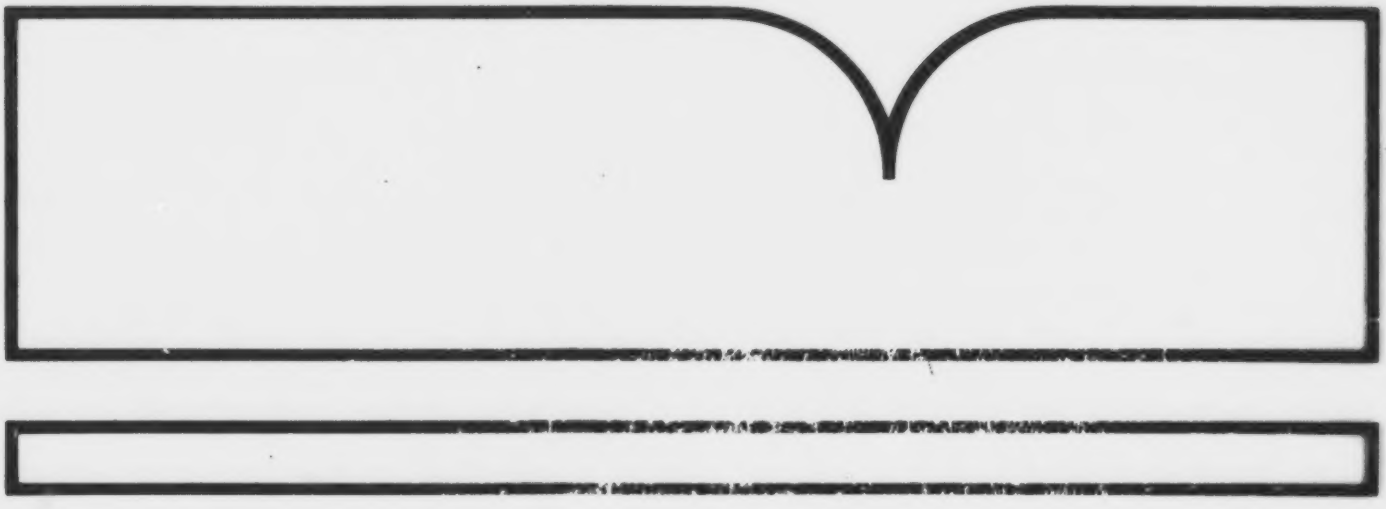

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LIQUID-LIQUID EXTRACTION OF TRACE LEVEL PESTICIDES FROM PROCESS STREAMS

by

G. V. Hiler

S. D. Cameron

S-CUBED
P. O. Box 1620
La Jolla, CA 92038-1620

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Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

AIR AND ENERGY ENGINEERING RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

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16. ABSTRACT The report describes the further resolution of the feasibility of a process (liquid-liquid extraction for the treatment of pesticide manufacturing wastewater) that had been shown by earlier research to be competitive with existing methods of treatment. Eight experiments were conducted using the Solvent Extraction of Organic Pesticides (SEXOP) process to treat process effluent samples of 2,4-D and bromacil. Process modifications designed to optimize the SEXOP system for treating these effluents were developed and tested. Gas chromatography was used to compare treated effluent with the untreated starting material. Pesticide extraction efficiencies were calculated: results show that pesticide removal in excess of 98% is attainable during initial operation, and 70% on a steady-state basis for a single-pass system for both samples tested. Staging of extraction units and increased solvent/water ratios would be expected to optimize steady-state efficiencies above 90%. An economic analysis, projecting engineering cost estimates for both a large and a small commercial-scale SEXOP process, shows that a projected large SEXOP plant should be able to process 301 million gal./yr of effluent at an estimated cost of about $2 per 1,000 gal.

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ABSTRACT

Research conducted previously by S-CUBED for IERL-RTP demonstrated that liquid-liquid extraction for the treatment of pesticide manufacturing wastewater is competitive with existing methods of treatment. The objective of this task was to resolve further the feasibility of this process.

A total of eight experiments were conducted using the Solvent Extraction of Organic Pesticides (SEXOP) process to treat process effluent samples of 2,4-D and bromacil. Process modifications designed to optimize the SEXOP system for treating these effluents were developed and tested.

Gas chromatographic analysis was used to compare treated effluent to the untreated starting material. Pesticide extraction efficiencies were calculated and are presented. Results show pesticide removal in excess of 98 percent is attainable during initial operation and 70 percent on a steady-state basis for a single pass system for both samples tested. Staging of extraction units and increased solvent/water ratios would be expected to optimize steady-state efficiencies above 90 percent.

An economic analysis projecting engineering cost estimates for both a large and a small commercial-scale SEXOP process is presented. A projected large SEXOP plant should be able to process 301 million gallons per year at an estimated cost of approximately $2 per 1,000 gallons.

This report was submitted in fulfillment of Contract No. 68-02-3629, Task 013, by S-CUBED under the sponsorship of the U.S. Environmental Protection Agency. This report covers a period from July 15, 1982 to April 15, 1983 and work was completed as of May 15, 1983.

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1.0 INTRODUCTION

The continued research to explore the feasibility of the extraction of pesticides from process streams, using high-volatility solvents and a liquid-liquid solvent extraction approach, is presented in this report. The Solvent Extraction of Organic Pesticides (SEXOP) process previously developed by S-CUBED (Ref. 1) was modified to explore the feasibility of treating two additional pesticide manufacturing effluent samples. This objective was carried out through the conduct of bench-scale studies using the SEXOP process apparatus and real-world effluent samples obtained from pesticide manufacturers.

Previous work conducted for IERL-RTP under cooperative agreement Contract CR807346 demonstrated that liquid-liquid extraction for the treatment of pesticide manufacturer wastewater was potentially less costly and more technically effective than existing technology and methods of treatment (Ref. 2). During the course of the S-CUBED/EPA cooperative agreement project a bench-scale SEXOP device was designed and constructed. In addition, wastewater samples from three pesticide manufacturers were acquired for the purpose of treatment by the SEXOP process using the bench-scale assembly.

The three samples acquired during the previous project were:

- One 55-gallon drum sample of DDT effluent from Montrose Chemical Corporation in Torrance, California
- One 55-gallon drum sample of 2,4-D effluent from Rhodia Inc. in Portland, Oregon
- One 55-gallon drum sample of bromacil effluent from E.I. DuPont de Nemours in LaPorte, Texas

The previous experimental work effort concentrated on research with the DDT wastewater. This report covers the continued research using the remaining two samples, 2,4-D and bromacil.

2.0 CONCLUSIONS

The purpose of this project was to continue bench-scale experimental research to resolve further the feasibility of the SEXOP process. This was accomplished through the conduct of eight bench-scale experiments using real-world 2,4-D and bromacil herbicide and pesticide manufacturer wastewaters.

A variable of significant importance explored during the current investigation is the extraction solvent. Hexane was the solvent used for the previous DDT extractions and also for initial experiments in this program. It was clear from the bromacil extraction efficiencies obtained in Runs 2 and 3 (80.7 percent and 58.8 percent, respectively, for the first half hour) that a different solvent with a higher partition coefficient would be necessary to attain the desired high extraction efficiency.

Conclusions based upon a review of solvent and solvent system literature, along with data obtained from previous screening extraction studies, resulted in a change of solvent from hexane to butyl chloride for extraction of wastewaters containing 2,4-D and bromacil. The greatly improved extraction efficiencies of Runs 4 and 5 (98.6 percent and 97.9 percent, respectively, for the first half hour) illustrate that the solvent has a very significant impact on extraction efficiency. Also, this illustrates that the partition coefficient continued to be an important variable, but due to the increased mechanical efficiency of the modified RDC, need not be nearly as high as the DDT/hexane system may have indicated. Moreover, it is clear from Runs 4 through 8 that cleanup of pesticide manufacturing wastewaters in the upper 90th percentile is possible, using a solvent that provides a relatively low K_p value. The K_p value for 2,4-D in butyl chloride is 5.7 compared to 28.7 for bromacil and 320,000 for DDT in hexane. Even so, extraction efficiencies for Runs 4 through 8 were all maintained above 95 percent during the first hour of operation.

With the present system configuration and methods of operation used, extraction efficiencies typically decline over time from some point until an equilibrium is attained. This was demonstrated in Run 8. In this seven-hour run the equilibrium point was reached at the 70 to 80 percent range.

Theoretically, this equilibrium is controlled by the partition coefficient achieved by the solvent, the solvent and water-flow rates, and the water/solvent volume ratio. Therefore, the level of decline and point of leveling off experienced in Run 8 can be adjusted by changing these parameters. While the water/solvent volume ratio was 4:1, a desirable ratio for running the RDC with the water phase dispersed in solvent, an increase in solvent/water flow rate and/or change to a solvent that yields an increased partition coefficient would almost certainly improve the overall efficiency and establish a higher level of equilibrium efficiency. From an economic standpoint, increasing the solvent flow rate over the water flow rate will not result in a very significant increase in operating expense, since the solvent is recycled and loss would continue to be minimal. Greater equipment size might be required for an increase in solvent flow rate.

The performance of the solvent recycle system currently used with the bench-scale apparatus was less than satisfactory. GC analysis of the condensed solvent showed some contamination, that if reused would certainly decrease efficiency. The source of contamination was traced to the stripper column. Due to the increased flow rates, this device tended to fill to capacity and spill over into the solvent reservoir. However, this is not considered a significant problem in the overall operation and potential of the process. The stripper length could be increased to accommodate the additional solvent flow to remedy this situation. Due to funding constraints this problem was not accorded significant attention. Also, solvent stripping and condensing hardware is commercially available so project funds were not allocated for development.

In summary, over the course of conducting eight experiments, essentially three process variables and two engineering modifications were investigated:

- Extraction solvent
- Process wastewater
- Water flow rate
- Rod agitators
- Settling reservoir

Results of this experimentation demonstrate several important advances in the process which include:

- High extraction efficiency is attainable for bromacil and 2,4-D effluent streams.
- The partition coefficient is a very important factor in achieving high efficiency. Mechanically induced column turbulence can offset low partition coefficients to produce high efficiencies.
- Extraction efficiency does decline over time but levels off at a steady state level that is dependent on flow rates, column turbulence, and solvent as partially demonstrated in Run 8.

A preliminary economic assessment was performed for the SEXOP process using butyl chloride as the extraction solvent and some engineering modifications incorporated in the experimental effort. The findings of this study did not significantly impact the economic analyses made in the prior project (Ref. 2). The results show that the cost of SEXOP technology compares favorably with alternative wastewater treatment options.

3.0 RECOMMENDATIONS

Considerably greater resolution has been attained through experimentation with the two additional wastewaters. Experience has also been acquired with an alternate solvent. This experience, in conjunction with data derived from previous studies, indicates that the SEXOP process could be applied to a wide range of organic pollutants provided the pollutant is characterized to determine optimum solvent or solvent systems. Continuation of research on alternate pesticide waste streams would develop even greater resolution in terms of the range of treatable effluents and versatility of extraction solvent systems available.

The last run of the series was performed to determine the steady-state extraction efficiency of the SEXOP system. Previous runs all indicated a slight decrease in extraction efficiency toward the end of the three-hour experiment. Run 8 shows that this decrease continues for a period of approximately three hours and then seems to level off. The steady-state extraction efficiency is important to the success of SEXOP as a continuous process and should be further characterized to determine optimum run conditions for any given solvent/wastewater system.

Evaluation of the SEXOP system at pilot-scale would provide further resolution of scale-up requirements and further document costs. A mobile pilot-plant could be fabricated on a truck or trailer bed to provide the capability to transport the entire system for on-site testing. This would also necessitate a self-contained power source along with the process equipment. The mobile pilot plant would be brought to the manufacturing facility and plumbed into the effluent stream to conduct on-site experimental runs and to evaluate applicability under real-world conditions.

Provision of multi-stage operation in the pilot unit and operation with higher solvent/water ratios would validate the contention that steady-state operation could be optimized to obtain high extraction efficiencies.

4.0 LIQUID-LIQUID EXTRACTION OF TRACE LEVEL PESTICIDES FROM PROCESS STREAMS

The following provides background, technical approach and results on the continued research into the feasibility of liquid-liquid extraction for removal of trace level pesticides from pesticide manufacturing wastewater. Further resolution of the process has been obtained through the analysis of bench-scale experiments conducted during the course of the research effort.

4.1 REVIEW OF THE BENCH-SCALE SEXOP SYSTEM

The SEXOP bench-scale system is a two-phase, counter current flow, liquid-liquid extraction device originally constructed for research conducted under IERL-RTP cooperative agreement Contract CR807346 (Ref. 2). Two-phase, counter-current flow involves a technique wherein a material of greater density is introduced at the top of the extractor unit, and a material of lesser density is introduced at the base. In this fashion, maximum liquid-liquid contact is obtained as both solutions migrate in opposing directions through a turbulent region of the extractor unit.

In addition to maximizing contact between the two liquid phases via counter-current flow, the SEXOP system incorporates a rotary disc contactor (RDC) design wherein a central shaft within the extractor chamber is fitted with a series of evenly spaced discs, which can be rotated at speeds of up to 1800 revolutions per minute. The driving force for the central shaft is a one-quarter horsepower, variable speed motor. The extractor chamber proper is constructed from 316 stainless steel segments and is approximately four feet (121.9 cm) high and three inches (7.6 cm) in diameter. Three of the segments are fitted with glass viewports to permit observation during the course of the experimental runs. Figure 4.1 shows the assembled RDC mounted in a walk-in hood.

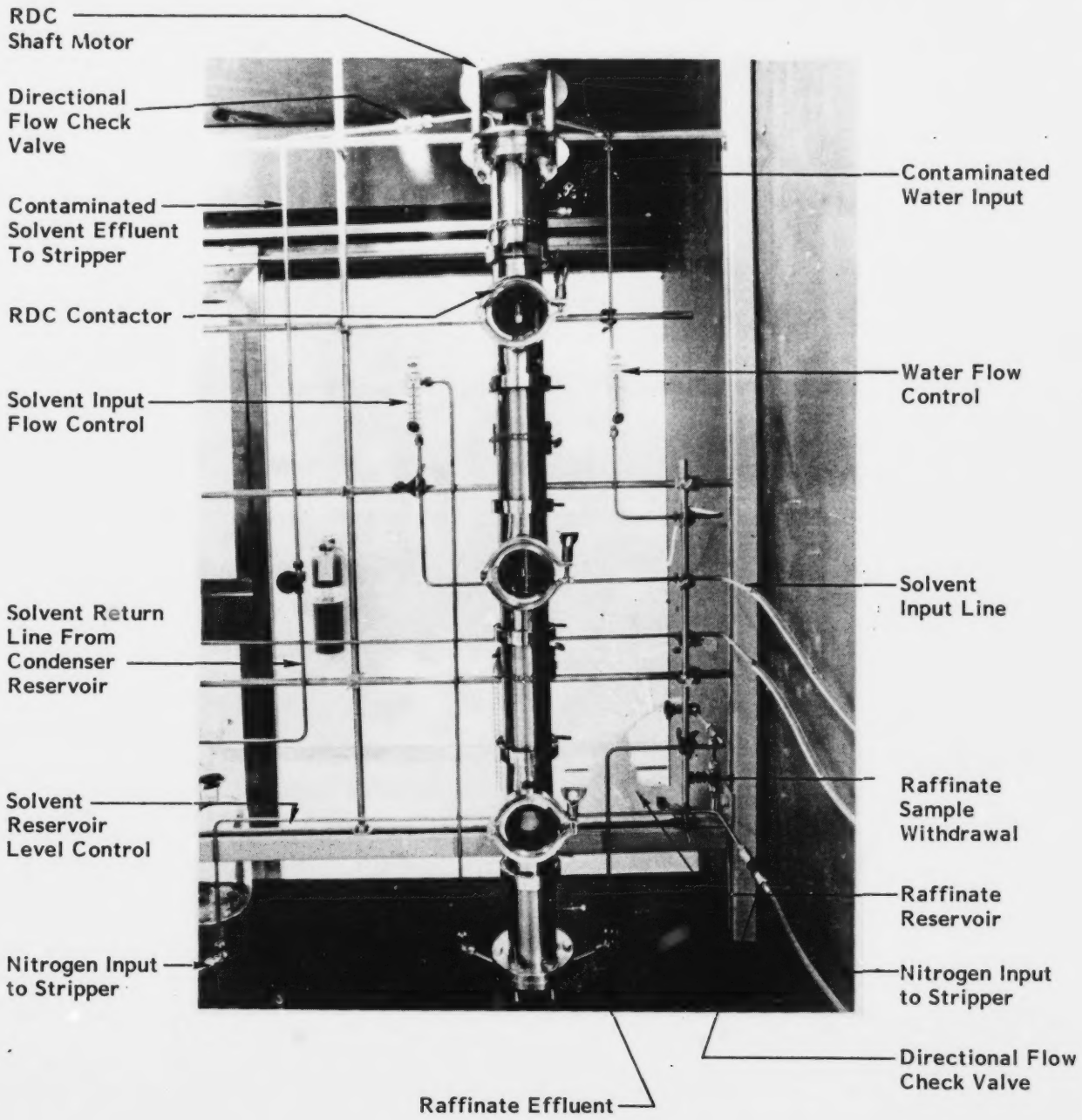

Figure 4.1 Rotary Disc Contactor With Attendant Plumbing Detail

Figure 4.2 illustrates the same assembly as did Figure 4.1 except that in Figure 4.2, the RDC is completely disassembled to show all component parts. Connected to the top and bottom end caps are stationary tubular shields that surround the rotating shaft and extend nine inches from each end plate of the RDC to reduce turbulence in these quiescent zones.

The pollutant-laden solvent generated during the SEXOP continuous-extraction process is routed to a counter-current solvent stripper. Figure 4.3 illustrates the solvent stripper which, when fully assembled, is four feet in length and three inches in diameter. It is made up of individual one-foot (30.5 cm) long sections enabling an increase or decrease in total length to provide optimum extraction efficiency. The material composing the packed bed of the column consists of 6 mm diameter glass beads.

Solvent from the RDC enters the upper section of the stripper column flowing downward through the packed bed. Nitrogen is introduced through the bottom flange, and due to a slight positive pressure differential, flows upward through the column.

Nitrogen and solvent vapor emitted from the top of the stripping column are routed to a water-cooled coil condenser. The solvent recovered is stored in a reservoir to be recycled into the RDC.

4.2 ENGINEERING MODIFICATIONS TO THE SEXOP SYSTEM

Prior to the commencement of the experimental runs using the RDC, an engineering optimization study was performed. The major difference of concern to the SEXOP process between the bromacil and 2,4-D wastewaters and the previously studied DDT wastewater is best illustrated in the partition coefficients relationship. The partition coefficient, Kp, is defined as:

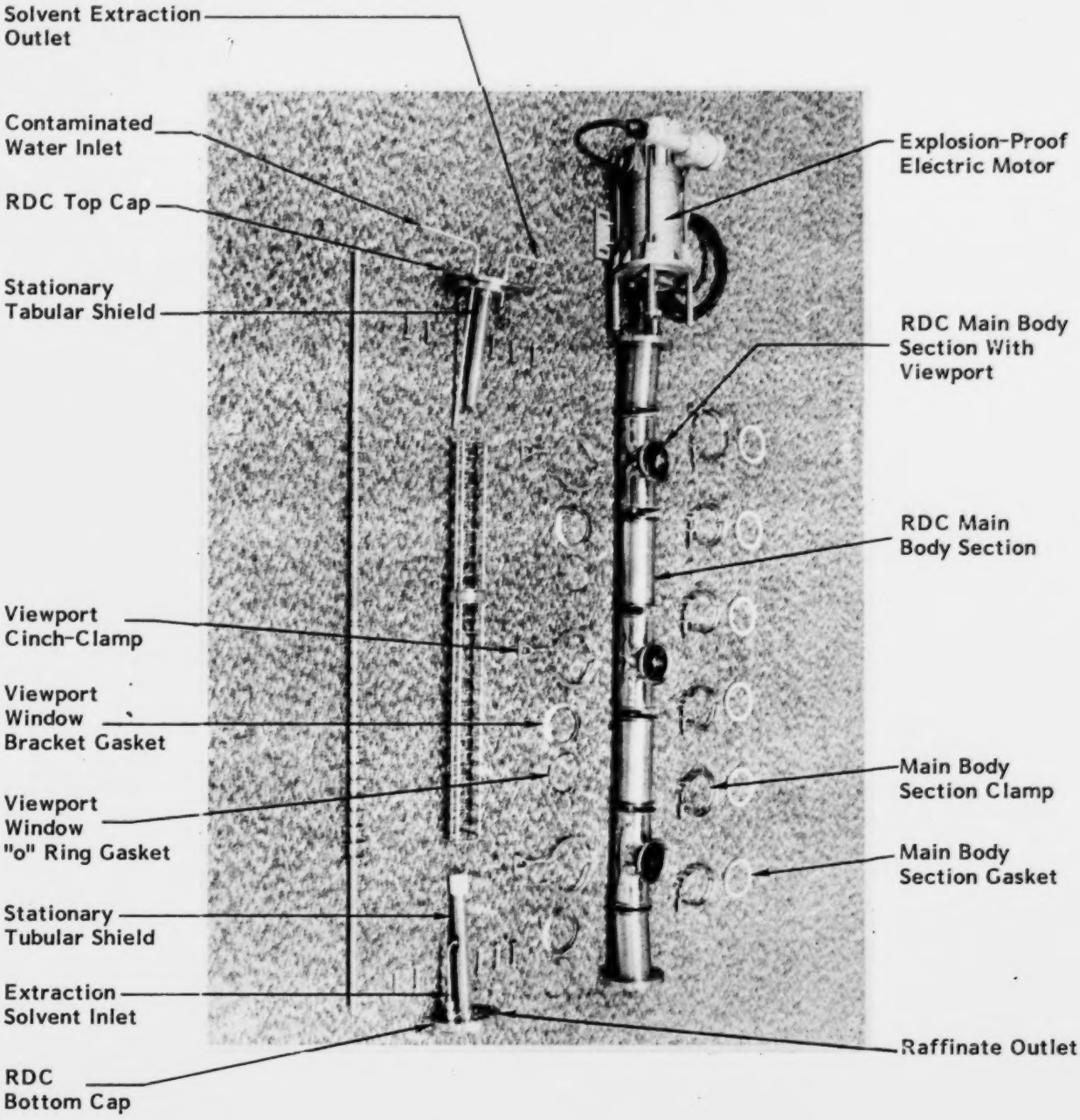

Figure 4.2 Fully Exploded View of the RDC

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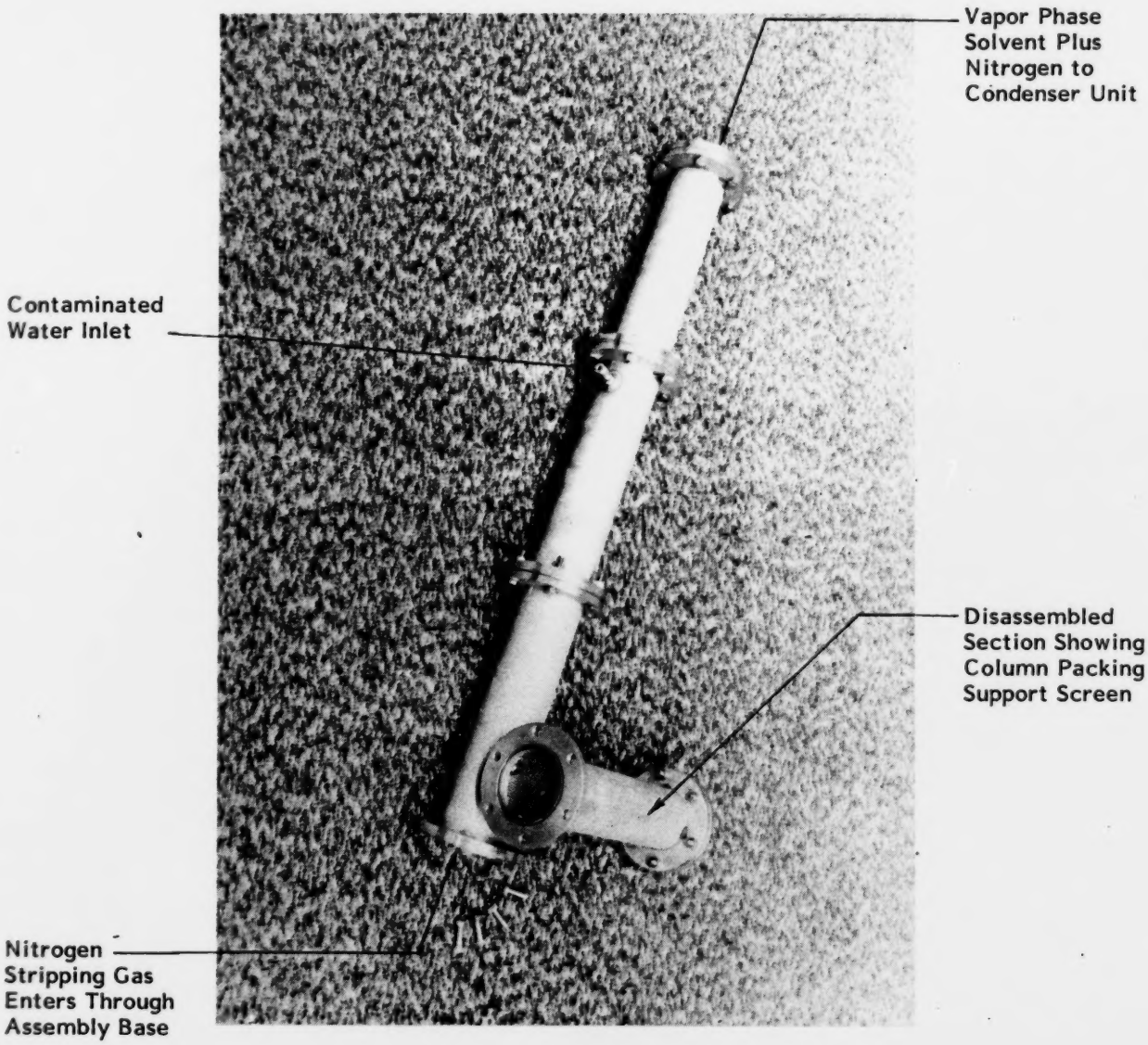

Figure 4.3 Counter-Current Solvent Stripper Shown With One Section of the Assembly Detached

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$$K_p = \frac{(S_B)_O}{(S_B)_W} \qquad (1)$$

where S_B is the solubility of the pollutant in the phase noted by the subscript O for organic (solvent) and W for aqueous.

The partition coefficient of a solvent/wastewater system constitutes the primary consideration in whether a solvent extraction process will be effective. The above formula for K_p is actually an idealized extension of Henry's Law which states that at sufficiently high dilution in a liquid solution, the fugacity of a nondissociating solute becomes proportional to its concentration. With respect to K_p, it may then be said that the concentrations of any singular molecular species in two phases which are in equilibrium with one another will bear a constant ratio to each other. This constant ratio will hold true, provided that the activity coefficients remain relatively constant.

The preceding is a simplified idealization which assumes no significant solute-solvent interactions. Empirical studies conducted by S-CUBED as well as other researchers, have shown that many organic compounds deviate considerably from ideal behavior in water and various solvents. Although this deviation often precludes a quantitative determination of K_p, it is, nevertheless, useful as a qualitative indicator. This project, as well as the previous research at S-CUBED, utilizes the theoretical K_p as a tool to aid in the selection of optimum solvent/pesticide systems as candidates for use during SEXOP runs.

During the previous research effort a series of screening extraction studies were conducted, the results of which were used to determine the theoretical K_p's of the solvent/pesticide systems of interest. These K_p values are presented in Table 4.1 and were used as background for the current study.

Referencing Table 4.1, note the rather broad range of theoretical K_p values for the various solvent/pesticide systems presented. Pre-

Table 4.1

PARTITION COEFFICIENT, K_p, OF PESTICIDES

	Hexane	Pentane	Isopropyl Ether	Ether	Butyl Chloride
DDT	320,000	270,000	230,000	960,000	370,000
Toxaphene	74,000	39,000	140,000	180,000	160,000
Chlordane	11,000	26,000	84,000	130,000	240,000
Norflurazon	17	27	61	190	200
Diuron	3.5	3.0	53.3	182	95.1
2,4-D	0.24	0.19	83.9	65.8	5.7
Bromacil	1.32	1.29	10.7	18.1	28.7
Glyphosate	0.111	0	0.048	0.109	0.030

vious experimentation with DDT resulted in a 99.9+ percent pesticide extraction efficiency using hexane as the extraction solvent in the SEXOP system. The theoretical K_p value of the hexane/DDT system is 320,000, while for bromacil the K_p values range from 1.29 up to 28.7. Considering the relatively low K_p value and comparing the previous results with DDT in the SEXOP apparatus, the unmodified RDC would propably produce marginal extraction efficiency. Therefore, it was hypothesized that a mechanism would be required to produce a greatly reduced droplet size and increased phase dispersion within the RDC. This would result in much greater solvent to water surface area contact, hence, theoretically higher extraction capabilities.

An engineering modification to the RDC disc structure designed to fulfill the above requirements was implemented. At the top and midpoint of the rotating shaft newly designed rod agitators were installed. These were constructed by tying together two of the rotating discs in eight equally spaced places with 8-32 stainless steel threaded rod and nuts. Figure 4.4 illustrates the nature of this modification.

Prior to the installation of the rod agitators, the water input tube was directed parallel to the rotating shaft with the end terminating perpendicular and slightly above the first stationary ring. To increase initial sample dispersion, the water input tube was bent toward the topmost agitator. The effect of this modification was to create a much finer spray as the wastewater entered the RDC system.

As a visual test of this modification, the system was carefully observed during experimental Run Number 1, an experiment using deionized water with the water phase dispersed. Prior to the rod agitator modification, individual solvent droplets could be visually resolved and observed migrating downward through the rotating-stationary disc cells. Observing the turbulence and accompanying solvent dispersion resulting from the engineering modification, there was no discernable individual droplet resolution in the active zone of the RDC. The regions of increased turbulence in the active zone had a cloudy appearance indicating the fine solvent breakup and decreased downward velocity.

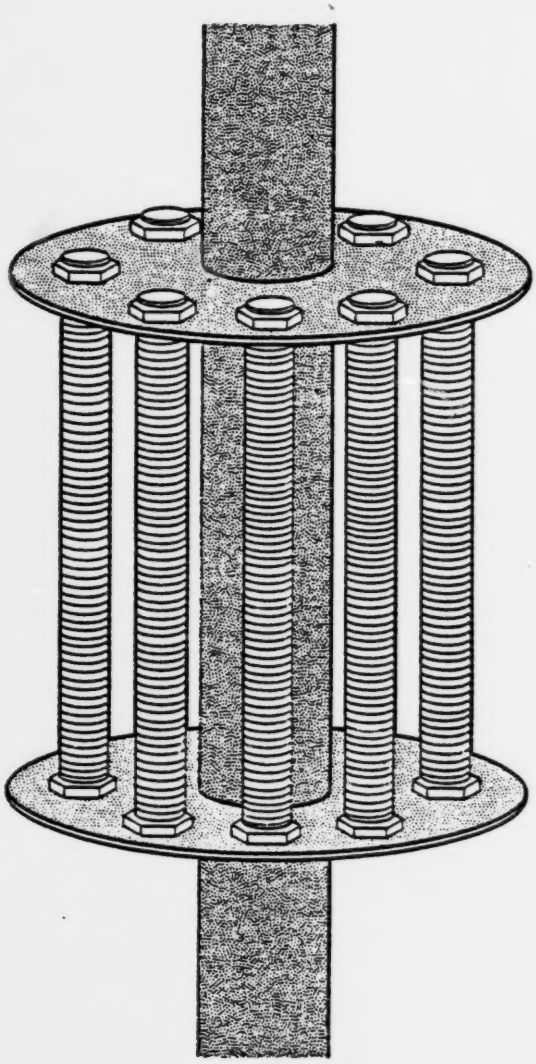


Figure 4.4 Rod Agitator

This greatly improved turbulence increased the potential for pesticide-laden solvent to become entrained in the treated wastewater. This would tend to have a negative effect on the results, in particular, if contaminated solvent should happen to mix with aliquots taken for analysis. Therefore, a second engineering modification was implemented to mitigate this potential problem. A 4-liter separatory funnel was installed as a settling reservoir to receive the water exiting the extractor unit. If any solvent should happen to exit the column with the treated water, further phase separation would take place in the reservoir.

In previous SEXOP experiments the possibility of solvent becoming entrained in the water exiting the unit was minimal since the solvent was dispersed through a relatively large volume of water. Treated water had ample time and volume for separation from the solvent.

In the current method of operation, however, most of the RDC volume is filled by the solvent with the treated water phase occupying a relatively small quiescent zone at the base of the column. Both the volume and time in which phase separation must occur are reduced. This, along with the greatly increased turbulence increases the potential for solvent becoming entrained in the treated water. With the settling reservoir in operation, the volume and time for phase separation are both increased.

The apparatus was set up so that water entering the reservoir runs down the side of the funnel in a small stream and collects at the bottom. Samples are taken each half hour by opening the stop-cock and draining up to 500 mL of water into a flask. Any solvent that may have entered the reservoir remains on top of the water and does not enter the sampling flask. Remaining fluid is drained into a large waste receptacle. The reservoir is then rinsed with deionized water to prevent mixing of water from consecutive sampling periods.

Over the course of eight runs, solvent entered the settling reservoir once during Run 2 and once during Run 7. Each time the separatory

funnel was effective in separating the phases, thereby preventing pesticide-laden solvent from contaminating the sample. Except for these two instances, water entering the reservoir was always free of solvent.

4.3 EXPERIMENTAL PROGRAM

A series of eight experimental runs were conducted on the bench-scale rotating disc contactor. The first run was a blank to check for contaminants in the SEXOP system. The second run was performed on a synthetic bromacil solution to establish a set of baseline parameters. Runs 3, 4, and 5 were done on real-world bromacil plant wastewater. Runs 6, 7, and 8 were conducted on real-world 2,4-D plant wastewater.

Bench-scale extractor data sheets were completed for each run documenting several engineering parameters such as motor speed, solvent flow rate and water flow rate. These data sheets are exhibited in Appendix A.

A typical run consists of the following procedures. Pesticide-laden water is stirred for 24 hours and allowed to settle for at least 1 hour prior to run initiation. The RDC column is then filled with the extraction solvent. Solvent and water flows are set at predetermined rates. The run is then initiated by turning the rotary disc column motor on at the top setting of 1800 rpm for maximum extraction efficiency. The water pump is turned on simultaneously, starting the flow of contaminated water into the top of the column. The water is immediately dispersed into fine droplets which migrate through the solvent and coalesce at the bottom of the column. Water is allowed to enter and displace the solvent out the top of the column in this fashion until the water:solvent ratio reaches about 1:4. The water/solvent interface is then visible at the lower view port. At this time, the water exit line at the bottom of the column is opened, and the solvent pump is turned on to begin fresh solvent migrating up from the bottom of the column through the water/solvent mixing zone. This steady state condition (water flow in equals water flow out; solvent flow in equals

solvent flow out) is maintained for the duration of the run, usually a total of three hours. Aliquots of treated water (100 mL) are taken every half hour from the time the mixer motor is started.

Contaminated solvent leaving the RDC passes to the stripper column where, in theory, it is vaporized, leaving contaminants behind. Vapor-phase solvent is then condensed in a separate vessel for reuse. For this effort, the stripper unit was not redesigned to compensate for (1) the relatively large quantities of solvent used (compared to the prior work, Ref. 2), or (2) the higher boiling solvents studied. As a consequence, through the course of experimental runs, the solvent recovery system was a constant problem due to its inability to vaporize the solvent rapidly enough to keep pace with contaminated solvent flow. Therefore, although the recovery system was in operation for most of the runs, recovered solvent was usually not reused for fear of cross contamination.

Starting material (raw wastewater) and aliquots of treated water were analyzed per EPA Method 633 for bromacil and EPA Method 615 for 2,4-D. Essentially, the analyses involved a hand shake solvent extraction of the 100-mL aqueous phase with three consecutive 50-mL portions of the reagent methylene chloride ($MeCl_2$). The three 50-mL methylene chloride extracts were combined and reduced to a volume of 10 mL by Kuderna-Danish concentration. The residual pesticide was quantitated using a gas chromatograph equipped with an 8-foot-long, 2-mm ID column containing three percent OV 101 on Supelcoport 100/120 and a Ni^{63} electron capture detector. Gas chromatographic data may be viewed in Appendix B.

The standard procedure consisted of diluting a 5-μL aliquot of the concentrated $MeCl_2$ extract to 10 mL with hexane, mixing, and then injecting a 1.00-μL aliquot into the gas chromatograph. SEXOP extraction efficiencies were then calculated by comparing the GC peak area of the starting material (S) with those of run aliquots (T_N) according to the following formula:

$$\text{Percent Efficiency} = 100 - \left(\frac{T_N}{S} \times 100\right) \quad (2)$$

Due to the wide range of extracted sample concentrations in Runs 4 through 8, varying quantities of the Kuderna-Danish concentrated $MeCl_2$ extract (KD-$MeCl_2$) were used to facilitate measurement of a statistically significant pesticide peak area. Consequently, the Percent Efficiency equation used for Runs 4 through 8 has been modified to accommodate the specific $MeCl_2$ extract volumes employed as shown in Equation (3):

$$\text{Percent Efficiency} = 100 - \left(\frac{T_N}{S} \times \frac{V_S}{V_T} \times 100\right) \quad (3)$$

where

V_S = Volume of KD-$MeCl_2$ extract used from starting material aliquot, µL.

V_T = Volume of KD-$MeCl_2$ used from test run aliquot, µL.

Quality assurance procedures outlined in Appendix D, required each series of samples analyzed to include a replicate, spike and laboratory blank. Calibration standards were also run each time to compensate for any variation in sensitivity of the GC.

Gas chromatography/mass spectrometry (GC/MS) analyses were conducted on both bromacil and 2,4-D process wastewater in order to confirm that neither pesticide had degraded significantly and to identify other constituents present. The data presented in Appendix C, indicates the bromacil process water did, in fact, contain bromacil in addition to the other identified constituents and the 2,4-D process water contains 2,4-D, seen in the mass spectrum, as well as other components.

4.3.1 SEXOP Runs

Run 1 was done as a field blank using deionized water dispersed in hexane, to ensure that there were no contaminants in the SEXOP system

and to establish a background "noise" level for the gas chromatography work. The run was conducted for three hours, with a water flow rate of 40 mL/min and a solvent flow rate of 20 mL/min. Solvent aliquots were taken every half hour in addition to the water aliquots. The gas chromatographic analysis was then performed simply by injecting a composite of the solvent samples directly into the GC. The chromatograph indicated a complete lack of contamination. Analysis of the water was, therefore, unnecessary, since any artifacts that would be of concern would be found in the solvent rather than the water.

Results of engineering modifications made since the previous series of SEXOP experiments were excellent. Dispersion of water through the solvent by agitators placed in the top and mid-column areas reduced the water to mist-size droplets. The 4-liter separatory funnel installed as a settling reservoir to accept the treated water greatly reduced the possibility of any solvent entrainment in the sample. If entrainment should happen to occur, however, it would be visible immediately in the glass reservoir.

Run 2 was conducted with a synthetic solution of bromacil (approximately 554 ppm in water) in order to establish a set of base-line results and operating parameters. As with Run 1, the extraction solvent was hexane, the water flow rate was 40 mL/min, and the solvent flow rate was 20 mL/min. Although there was a period of about 15 min in which hexane was not being pumped, the run was successful in providing baseline information.

As shown in Table 4.2, T_0 taken at 1/2 hour represents the best-case pesticide extraction efficiency for Run 2 at 80.7 percent cleanup. In subsequent aliquots efficiencies steadily decreased to 30.2 percent at the end of three hours. This trend was expected and can be explained as follows: The RDC is initially charged with fresh solvent, and as the wastewater comes in contact with the solvent, the pesticide begins to move from the aqueous phase to the organic phase. But the ability of the solvent to extract the pesticide is limited by the relatively low

Table 4.2

RUN 2 - RESULTS

Sample	GC Peak Area	Pesticide Extraction Efficiency (%)
S	103,137	--
T_0	19,928	80.7
T_1	39,536	61.7
T_2	50,961	50.6
T_3	61,159	40.7
T_4	65,390	36.6
T_5	71,967	30.2

Table 4.3

RUN 3 - RESULTS

Sample	GC Peak Area	Pesticide Extraction Efficiency (%)
S	12,879	--
T_0	5,303	58.8
T_1	7,050	45.3
T_2	9,554	25.8
T_3	10,794	16.2
T_4	10,923	15.2
T_5	12,834	0.3

partition coefficient (K_p = 1.32) and the relative flow rates. Therefore, in this case, as the solvent became more laden with pesticide, the pesticide extraction efficiency decreased.

Real-world, bromacil plant wastewater was used to perform Run 3. Operating conditions were unchanged from Run 2, except that the solvent recovery system was in operation and returning solvent to the RDC system. Difficulties developed with the hexane pump on two occasions due to air entering the line. The RDC was shut off briefly the first time to eliminate the air. The second time the air was purged into the RDC column. This resulted in some foaming for a short period.

Run 3 pesticide extraction efficiencies, shown in Table 4.3, were again low, starting at 58.8 percent at the first 1/2 hour and finishing at 0.3 percent after 3 hours. However, efficiencies might have been better had there been no pump problems and no recycling of solvent. At the end of the run, solvent in the condenser reservoir (returning hexane to the RDC) was observed to have an amber cast similar to that of the bromacil wastewater. Injection of this solvent into the GC showed heavy contamination.

In spite of technical malfunctions during Run 3, the low partition coefficient (K_p) of bromacil with hexane was probably responsible, more than any other factor, for the poor efficiencies of Runs 2 and 3. Bromacil is not significantly more soluble in hexane (950 ppm) than in water (717.7 ppm). Therefore, a change in extraction solvent was indicated and butyl chloride was decided upon as the best choice. The solubility of bromacil in butyl chloride is 20,583 ppm resulting in a K_p value of 28.7. The added cost of $.80/gal and a 9.4°C higher boiling point were compensated by the slightly lower solubility in water and the much greater affinity for bromacil.

As presented in Table 4.4, the resulting significant improvement in pesticide extraction efficiencies of Run 4 were even better than expected; 98.6 percent for the first half hour, dropping only to 90.2

percent at the end of three hours. Recovered solvent was not recycled to the RDC as it was in Run 3. However, foaming was observed as a result of air entering the column. Also, a small solvent leak developed at the top RDC bearing during the last 10 minutes of the run. These difficulties apparently had little detrimental effect on the results. It should be noted that in Table 4.4 and for subsequent Tables 4.5 through 4.8, Equation (3) was used to calculate the pesticide extraction efficiency and the third column in these tables reports the specific volume of KD-concentrated methylene chloride extract used in the analysis.

In an effort to duplicate the pesticide extraction efficiencies of Run 4, all experimental parameters remained the same for Run 5. Except for some brief periods of foaming and some solvent leakage from the top bearing, the run went smoothly. Pesticide extraction efficiences were lower than in Run 4, starting at 97.9 percent for the first half hour, falling to 79.4 percent after 3 hours (Table 4.5).

The shaft seal leak on top of the RDC proved to be a continuing annoyance in the remaining experiments. This was the case in spite of the fact that a new seal was installed before each of the remaining runs. Apparently, the problem resulted from the incompatibility of butyl chloride with the seal material. Moreover, this may have been compounded by the acidic 2,4-D wastewater (pH 2), used for Runs 6, 7, and 8. In each of these runs, the solvent leak was slowed considerably by directing the solvent exit line into an open receptacle, thereby reducing the RDC internal pressure to near zero. Although this allowed a few bubbles of air to enter the column occasionally, it had no other apparent adverse effect on the actual performance of the RDC or on the results.

Run 6 was the first of the series to be performed on the 2,4-D wastewater. All other operating parameters were unchanged from Runs 4 and 5. In addition to the shaft seal leak, the water flow meter also began leaking. Attempts to remedy this problem were unsuccessful, and

Table 4.4

RUN 4 - RESULTS

Sample	GC Peak Area	KD-$MeCl_2$ Extract (μL)	Pesticide Extraction Efficiency (%)
S	54,352	5	--
T_0	22,479	150	98.6
T_1	29,502	100	97.3
T_2	25,764	50	95.3
T_3	38,518	50	92.9
T_4	44,852	50	91.7
T_5	53,032	50	90.2

Table 4.5

RUN 5 - RESULTS

Sample	GC Peak Area	KD-$MeCl_2$ Extract (μL)	Pesticide Extraction Efficiency (%)
S	13,697	2	--
T_0	22,063	150	97.9
T_1	15,752	50	95.4
T_2	11,655	25	93.2
T_3	14,411	20	89.5
T_4	20,877	20	84.8
T_5	35,340	25	79.4

Table 4.6

RUN 6 - RESULTS

Sample	GC Peak Area	KD-$MeCl_2$ Extract (μL)	Pesticide Extraction Efficiency (%)
S	8,716	7	--
T_0	5,383	500	99.1
T_1	7,010	400	98.6
T_2	6,745	200	97.3
T_3	8,459	150	95.5
T_4	8,294	150	95.6

Table 4.7

RUN 7 - RESULTS

Sample	GC Peak Area	KD-$MeCl_2$ Extract (μL)	Pesticide Extraction Efficiency (%)
S	5,531	15	--
T_0	6,088	1,150	98.9
T_1	5,759	500	96.9
T_2	4,857	700	93.4
T_3	5,605	700	92.4
T_4	7,108	200	90.4
T_5	6,208	150	88.8

Table 4.8

RUN 8 - RESULTS

Sample	GC Peak Area	KD-$MeCl_2$ Extract (μL)	Pesticide Extraction Efficiency (%)
S	5,622	20	--
T_0	8,557	2,000	98.5
T_1	7,109	500	94.9
T_2	6,977	200	87.6
T_3	6,944	150	83.5
T_4	8,404	150	80.1
T_5	5,921	100	78.9
T_6	5,114	100	81.8
T_7	7,150	100	74.6
T_8	7,183	100	74.4
T_9	6,327	100	75.7
T_{10}	7,430	100	73.6
T_{11}	6,747	100	76.0
T_{12}	3,978	100	85.8
T_{13}	8,134	100	71.1

the run was terminated at the T_3 sampling time. Sample T_4 was then taken from the treated water remaining in the bottom of the RDC. As presented in Table 4.6, pesticide extraction efficiencies proved to be quite good with 99.1 percent for T_0, declining only to 95.5 percent after two hours for T_3 and 95.6 percent for T_4.

Considering such favorable pesticide extraction efficiencies for Run 6, an attempt to improve the economic efficiency of the system was made in Run 7 by doubling the water flow rate from 40 mL/min to 80 mL/min. Two new glass flow meters were installed in order to control better water and solvent flow rates. Much foaming was observed in the turbulent areas of the RDC creating an emulsion at the water/solvent interface. This interface is generally held in view at the lower port by adjusting the water exit flow rate manually with a valve. However, the interface was not discernable due to the emulsion, and when the run was completed an hour later, the interface had risen above the top port. The water/solvent volume ratio increased from 1:4 to 4:1.

In spite of the variable water/solvent volume ratio and considering the doubled water flow rate, results were nevertheless quite good. As shown in Table 4.7, pesticide extraction efficiencies started at 98.9 percent for the first half hour and finished at 88.8 percent after 3 hours. A nearly-linear, efficiency decline depicted in Figure 4.5 did not seem to reflect the emulsion or the volume ratio problems.

As discussed earlier, this downward trend in efficiencies over time is expected. The initial volume of solvent is clean, but as it is contacted with the wastewater and begins absorbing the pesticide, its extracting ability declines. Theoretically, efficiencies will decline to an equilibrium (steady state) point depending on the flow rates, the water/solvent volume ratio, and the partition coefficient.

In an attempt to establish this steady state point, Run 8 was conducted for a period of seven hours. Another flow meter was installed to regulate the water exit flow, thereby eliminating any water/solvent

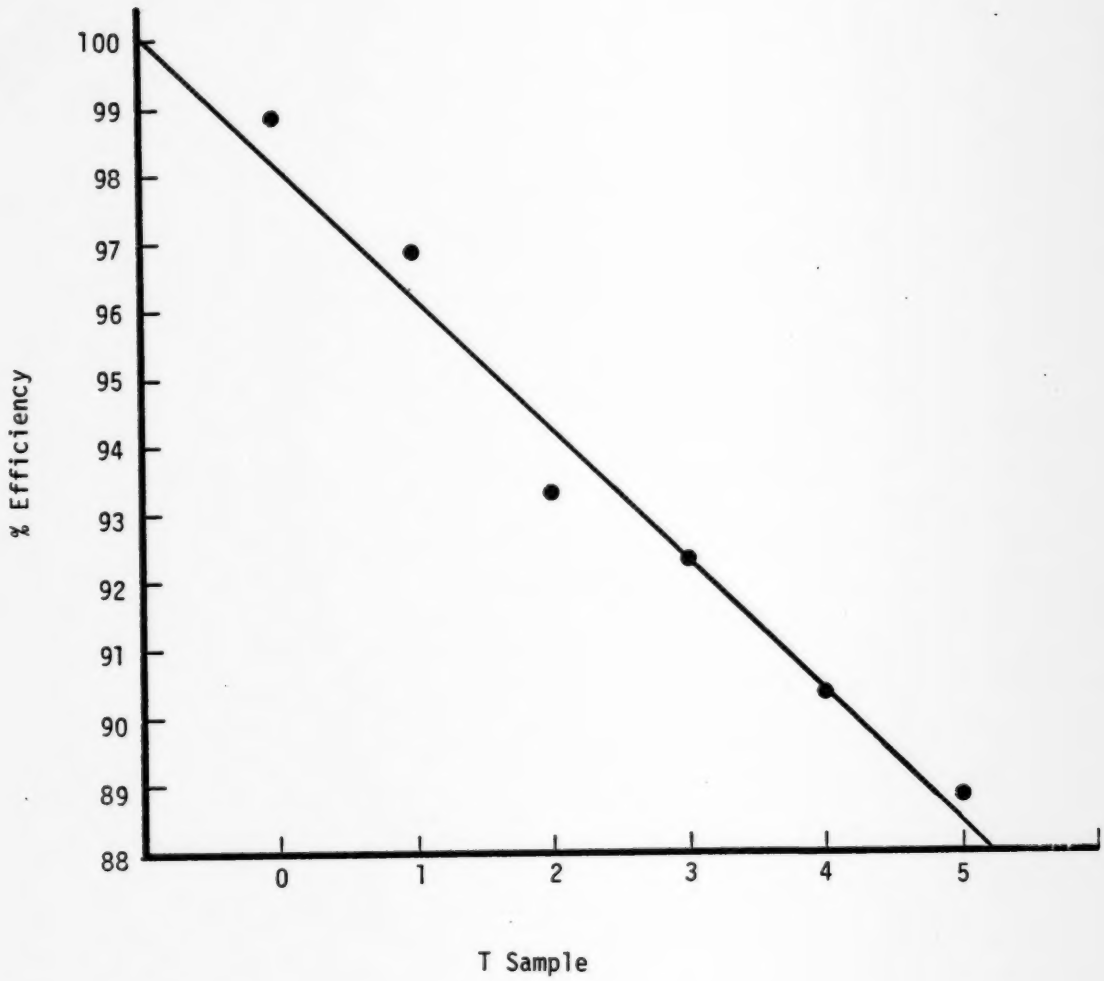


Figure 4.5 Run 7 Pesticide Extraction Efficiency vs. Sample Time

volume ratio problem. Otherwise, all other operating parameters were the same as those of Run 7. Although the run went very smoothly, with no foaming or emulsion problems, efficiencies were not quite as impressive as those of Run 7. As presented in Table 4.8, the decline was more rapid, dropping from 98.5 percent at T_0 to 78.9 percent at T_5. A leveling out began to occur around T_4 in the 80 percent to mid 70 percent range, shown graphically in Figure 4.6. It appears that the steady state condition is attained somewhere in this region.

Table 4.9 summarizes all pesticide extraction efficiencies and corresponding SEXOP variables. The eight experimental runs have tested two engineering modifications and three SEXOP variables, and explored one characteristic of the process distinctive to the current method of operation.

In addition to confirming that the RDC system was free of contaminants, Run 1 served to evaluate the engineering modifications. The rod agitators reduced the incoming stream of wastewater to a fine mist, providing excellent dispersion of the water through the solvent. The settling reservoir, designed to provide additional time and volume for separation of water and solvent phases, appeared to minimize the possibility of contaminating the treated water with solvent.

The first SEXOP variable tested was the extraction solvent. Hexane was the initial solvent due to its attractiveness from an economic standpoint and in hopes that its low K_p for the pesticides of interest would be compensated for by the high efficiency turbulence of the RDC column. Runs 2 and 3 both demonstrated, however, that hexane was inadequate for extracting bromacil from water. Butyl chloride provided greatly improved results over hexane as shown in Runs 4 and 5.

The second variable tested was the process wastewater. Runs 3, 4, and 5 were conducted on bromacil wastewater. The remaining Runs 6, 7, and 8 were performed on 2,4-D wastewater. Butyl chloride proved to be a far more satisfactory extraction solvent for both pesticides than hexane.

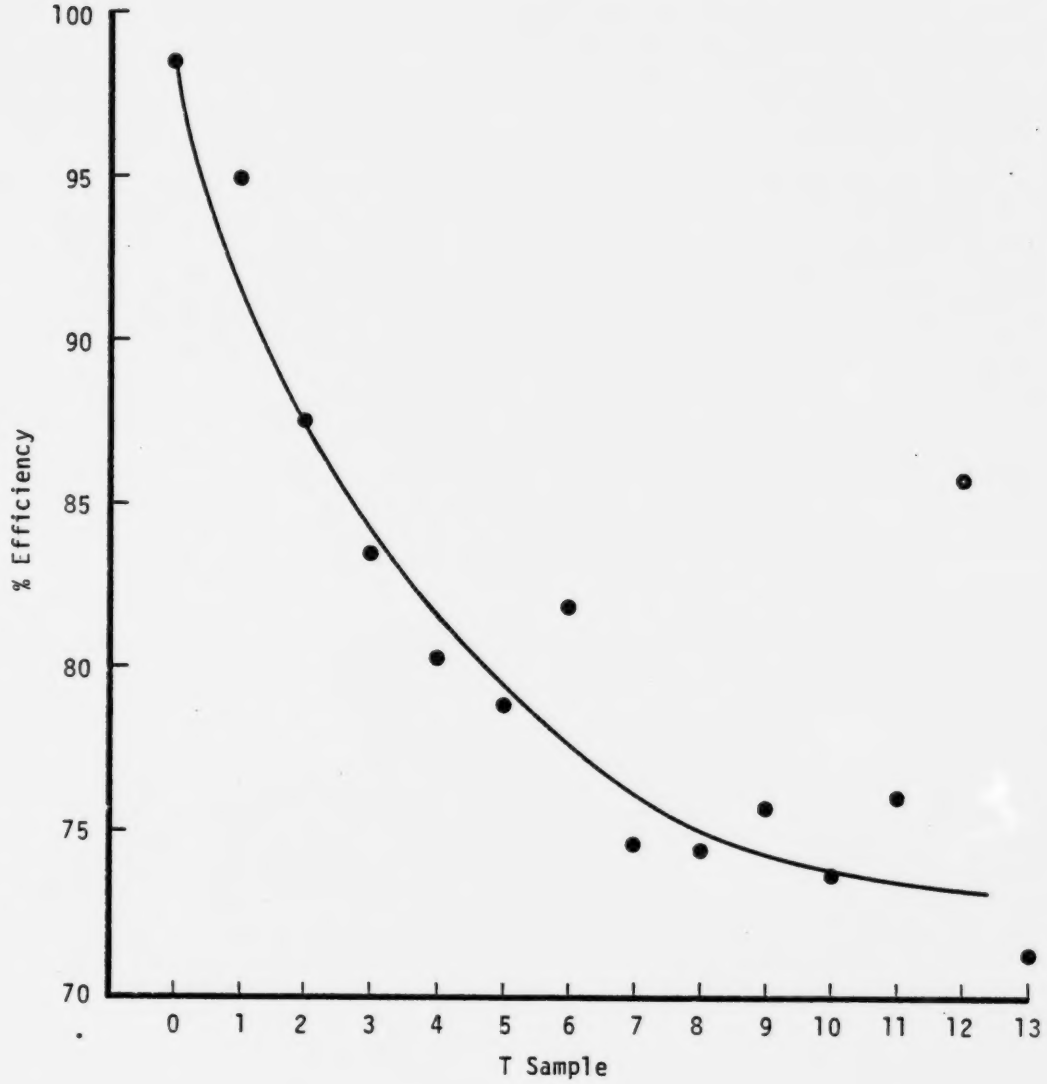


Figure 4.6 Run 8 Pesticide Extraction Efficiency vs. Sample Time

Table 4.9

SUMMARY OF PROJECT EXPERIMENTS[a,b,c]

Run No.	Pesticide Extraction Efficiency (%) T_0	T_1	T_2	T_3	T_4	T_5	Aqueous Feed	Solvent	Water Flow Rate ml/min	Water/ Solvent Flow Ratio	Water/ Solvent Volume Ratio	Exchanges Per Hour
1	--	--	--	--	--	--	Deionized Water	Hexane	40	2:1	1:4	0.76
2	80.7	61.7	50.6	40.7	36.6	30.2	Synthetic Bromacil Solution	Hexane	40	2:1	1:4	0.76
3	58.8	45.3	25.8	16.2	15.2	0.3	Bromacil Plant Wastewater	Hexane	40	2:1	1:4	0.76
4	98.6	97.3	95.3	92.9	91.7	90.2	Bromacil Plant Wastewater	Butyl Chloride	40	2:1	1:4	0.76
5	97.9	95.4	93.2	89.5	84.8	79.4	Bromacil Plant Wastewater	Butyl Chloride	40	2:1	1:4	0.76
6	99.1	98.6	97.3	95.5	95.6	--	2,4-D Plant Wastewater	Butyl Chloride	40	2:1	1:4	0.76
7	98.9	96.9	93.4	92.4	90.4	88.8	2,4-D Plant Wastewater	Butyl Chloride	40	4:1	1:4-4:1	1.27
8*	98.5	94.9	87.6	83.5	80.1	78.9	2,4-D Plant Wastewater	Butyl Chloride	40	4:1	1:4	1.27

*Run 8 additional extraction efficiencies:

Sample Number	T_6	T_7	T_8	T_9	T_{10}	T_{11}	T_{12}	T_{13}
Extraction Efficiency (%)	81.8	74.6	74.4	75.7	73.6	76.0	85.8	71.1

a) A typical run consists of the following:

(1) Fill the RDC column with solvent. (2) Start the mixer motor and wastewater input allowing the water to displace approximately 1/5 of the solvent volume. (3) When the water/solvent volume ratio reaches 1.5, start the solvent flow in and water flow out. (4) This steady state condition is maintained until 3 hours have elapsed from the time the mixer motor and wastewater input was started. (5) Aliquots of treated water are taken every half-hour.

b) Motor speed = 1800 rpm.

c) Solvent flow rate = 20 ml/min.

Water flow rate became the third variable of investigation. This was doubled in Run 7 in order to improve the economic efficiency of the system. Results were very good; showing a typical linear decline in efficiencies over the three-hour period.

This led to the final run which explored this efficiency decline, a characteristic of the process distinctive of the operational mode in which the water phase is dispersed in the solvent phase. Run 8, conducted for seven hours, demonstrated that the expected steady state condition is reached after 2.5 to 3.0 hours of continuous extraction. It should be noted that although only a 70 percent steady state extraction efficiency was demonstrated in this study for the specifically designed bench-scale unit. It would be relatively straightforward to stage these units to enhance the overall efficiency. For example, a two-stage unit would theoretically reduce the raffinate concentration to 9 percent corresponding to a 91 percent extraction efficiency. The point to be made is that by judicious engineering design it would be possible to optimize the removal efficiency.

4.4 ECONOMIC ANALYSIS

During the conduct of the previously cited S-CUBED/EPA cooperative agreement project, substantial attention was focused on deriving engineering cost estimates for commercial-scale SEXOP systems capable of treating a 91,000-gallon-per-day effluent stream and a 910,000-gallon-per-day effluent stream. These two commercial-scale sizes represent factors of 1,000 and 10,000 times the volume of the bench-scale device used in the conduct of the previously described experiments.

The solvent change and engineering modificaton which have been made during the course of this project are not of a nature which would significantly impact the previously made estimates. Therefore, the following estimated costs are essentially unchanged from the previous report. These costs represent only general approximations but are sufficiently accurate for the purpose of comparative analysis.

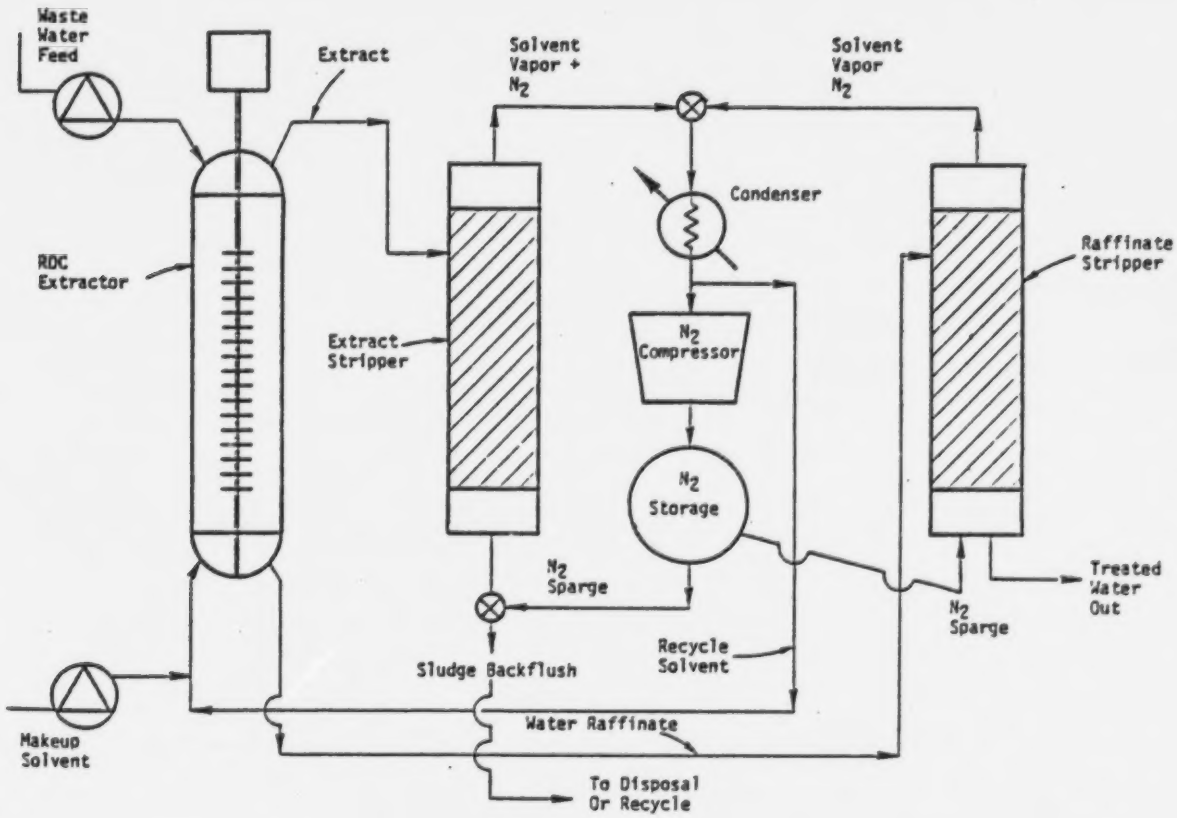
4.4.1 Cost Models for Commercial-Scale SEXOP Processes

The component parts which would comprise a commercial-scale SEXOP process are integrated schematically in Figure 4.7. Located beneath this figure is a list of the major captial equipment items which would require an initial expenditure outlay for plant construction. The same components would be required for both a small and large commercial process; only the scale would differ.

For the purpose of this discussion a small commercial-scale process would generate a 91,000-gallon-per-day effluent stream and large commercial-scale process would generate a 910,000 gallon-per-day effluent stream. These two commercial-scale sizes represent factors of 1,000 and 10,000 times the volume of the bench-scale device fabricated for this study.

An engineering cost estimate has been derived for both of the above commercial-scale model sizes, which presents projections for both capital equipment and operation and maintenance (O&M) parameters. Capital equipment projections (including a bottom line O&M summary) is presented in Table 4.10. A breakdown of estimated O&M cost projections is presented in Table 4.11. Sources used to derive the presented costs are cited in References 3-15. Projected costs in Tables 4.10 and 4.11 represent what is generally called an order-of-magnitude engineering cost estimate with an error range $\pm$30 percent. This type of estimate is satisfactory for the comparative purpose of this project which essentially involves the determination of economic feasibility of solvent extraction technology vis-a-vis carbon adsorption. Estimates of greater accuracy would be possible based on current knowledge, however, these would be extremely time consuming and outside the scope of this project.

All capital costs cited in connection with this study represent "installed costs" which include the initial purchase cost plus all charges incurred while the equipment is being connected into the plant system and made ready for operation.



CAPITAL EQUIPMENT REQUIRING
INITIAL EXPENDITURE OUTLAY

1) Waste Water Feed Pump
2) Makeup Solvent Feed Pump
3) RDC Shaft Motor
4) RDC Extractor
5) Extract Stripper
6) Solvent Vapor Condensor
7) N_2 Compressor
8) N_2 Storage Vessel
9) Raffinate Stripper

Figure 4.7 Commercial-Scale SEXOP Process

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Table 4.10

CAPITAL EQUIPMENT REQUIRING INITIAL EXPENDITURE OUTLAY - SOLVENT EXTRACTION

91,000 GPD Plant		910,000 GPD Plant	
Component Description	Cost $[1]	Component Description	Cost $[1]
1) Wastewater feed pump (not explosion proof; 10 HP motor; 3,800 gal/hr; 60 gal/min	7,176	1) Wastewater feed pump (not explosion proof); 100 HP motor; 38,000 gal/hr; 630 gal/min	20,503
2) Makeup solvent feed pump (explosion proof) 1 HP motor; 380 gal/hr; 6 gal/min	5,125	2) Makeup solvent feed pump (explosion proof) 10 HP motor; 3,800 gal/hr; 60 gal/min	10,252
3) RDC shaft motor (explosion proof) 1 HP	200	3) RDC shaft motor (explosion proof) 10 HP	1,025
4) RDC extraction vessel (with shaft & discs) 1,300 gal; 170 ft^3	34,855	4) RDC extraction vessel (with shaft & discs) 13,000 gal; 1,700 ft^3	210,158
5) Extract stripper - 1,000 gal; 140 ft^3; includes stripper tower packing	23,579	5) Extract stripper - 11,000 gal; 1,400 ft^3; includes stripper tower packing	86,113
6) Solvent vapor condenser	16,403	6) Solvent vapor condenser	164,025
7) N_2 compressor - 300 ft^3/min	23,579	7) N_2 compressor - 3,3000 ft^3/min	112,768
8) N_2 storage vessel 50 ft^3	15,377	8) N_2 storage vessel 500 ft^3	153,774
9) Raffinate stripper - 1,000 gal; 140 ft^3; includes stripper tower packing	23,579	9) Raffinate stripper - 11,000 gal; 14,000 ft^3; includes stripper tower packing	86,113
TOTAL	149,873	TOTAL	844,731

[1]All estimates represent "installed costs" corrected to 1984 dollars.

Table 4.11

SUMMARY OF FIRST YEAR O&M COST FOR SOLVENT EXTRACTION

Small Plant (91,000 GPD)		Large Plant (910,000 GPD)	
O&M Category	Cost $	O&M Category	Cost $
1) Initial solvent charge + makeup	5,000	1) Initial solvent charge + makeup	56,000
2) Labor (administrative and technical mix)	20,000	2) Labor (administrative and technical mix)	40,000
3) Maintenance	15,000	3) Maintenance	30,000
4) Electrical (6.3×10^5 KWH)	44,000	4) Electrical (4.4×10^6 KWH)	308,000
5) Debt service and amortization*	30,195	5) Debt service and amortization*	169,254
6) Real estate taxes and insurance**	2,997	6) Real estate taxes and insurance**	16,895
TOTAL	117,192	TOTAL	620,149

*At 10% interest over seven years.
**At 2% of the total capital.

These installed costs were determined using the Guthrie module approach (Ref. 6). This approach involves the determination of a "Base Cost" for each major piece of processing equipment multiplied by certain "Adjustment Factors" and a "Bare Module Factor". The base cost and each of the accompanying factors is specific to the type of equipment under consideration (i.e., each type of equipment has a different set of factors). Following are brief definitions of these key costing relationships.

- Base Cost

  Derived from costing graphs consisting of plots over a broad general range for each type of major equipment. For example, base costs for process vessels were derived from a nomograph plotting diameter against height or length against vertical or horizontal fabrication to determine FOB equipment cost in dollars.

- Adjustment Factors

  Consider parameters such as material of construction, equipment operating limits, and adjustments to current prices through use of an equipment cost inflation index. These adjustment factors are multiplied by the base cost as follows:

  Purchased Equipment $ = [Base Cost $(F_m)(F_o)$ Index]

  where: F_m is a material of construction factor and
  F_o is an operating limit factor.

  The index used for this study was the Marshall and Swift (M&S) Process Industry Equipment Index.

- Bare Module Factor

  Includes all the direct and indirect cost elements in the process module; and, used as a multiplier on equipment cost, it is a measure of the dollars required to integrate single or multiple pieces of equipment into a particular process circuit. This factor can vary between 2.38 and 3.64 depending on the type of equipment under consideration.

Electrical energy requirements pertinent to the operation and maintenance (O&M) projections are based on $0.07/KWH. Costs for the two SEXOP models are based on extrapolations of the bench-scale device which consists of a 4.8 liter (1.267 gallon), rotary disc contactor

(RDC) extraction vessel and a 4.17 liter (1.1 gallon) solvent stripper system. Based on bench-scale runs which have produced favorable results on the RDC extraction system, an exchange rate of three exchanges per hour was selected as the nominal process flow for the presented models.

Other process component flows, specifications and volumes for both small and large commercial-scale models are presented in the Table 4.10 capital equipment listing. Generally, these projections are based on actual run criteria for the bench-scale process. The single exception to this is the raffinate stripper which does not have a counterpart in the bench scale system. Design, flow and capacity specifications for this device may be conveniently extrapolated, however, as a function of treated effluent flow from the RDC extractor.

Operation and maintenance (O&M) costs for a commercial-scale SEXOP process are projected as being minimal because the process is predominantly a closed-loop system requiring only minor periodic adjustment.

The initial solvent charge consists of sufficient volume to allow for a four-hour run backlog plus a loss of 20 percent of this stock over a one-year period at a commercial cost for butyl chloride of $3.20 per gallon. Insofar as the solvent is recycled and the raffinate is stripped, solvent losses are expected to be minimal. Also, because the process is designed to operate at ambient temperature, electrical energy requirements are relegated solely to the operation of pumps, compressor and minor utility needs.

Since the SEXOP process is predominantly a closed loop system, labor allocations are primarily associated with routine maintenance activities.

At its current stage of development, the projected O&M costs must necessarily be conjectural. Repeated laboratory runs with the bench-scale system have, however, consistently verified the assumptions used in projecting the costs.

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APPENDIX A

BENCH-SCALE EXTRACTOR DATA SHEETS

BENCH SCALE EXTRACTOR
DATA SHEET

RUN # 1
DATE 8/16/82
DESCRIPTION Blank H_2O

SAMPLE	TIME	MOTOR[1] SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	9:10	100				4740	40			0.51
T_0	9:40	100			20	4740	40	1200	2:1	0.76
T_1	10:10	100			20	5340	40	2400	2:1	0.76
T_2	10:40	100			20	5940	40	3600	2:1	0.76
T_3	11:10	100			20	6540	40	4800	2:1	0.76
T_4	11:40	100			20	7140	40	6000	2:1	0.76
T_5	12:10	100			20	7740	40	7200	2:1	0.76

COMMENTS: Deionized water dispersed in hexane to check for contaminates in extractor system. Solvent recovery system not in operation, therefore nitrogen is not used.

[1]Control box speed setting represents 1800 rpm.

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 2
DATE 8/27/82
DESCRIPTION Synthetic Bromacil

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	10:09	100				4740	40			0.51
T_0	10:39	100				4740	40	1200		0.51
T_1	11:09	100			20	5080	40	2400	2:1	0.76
T_2	11:39	100			20	5680	40	3600	2:1	0.76
T_3	12:09	100			20	6280	40	4800	2:1	0.76
T_4	12:39	100			20	6880	40	6000	2:1	0.76
T_5	1:09	100			20	7480	40	7200	2:1	0.76

COMMENTS: Synthetic bromacil solution dispersed in hexane. Solvent recovery system not in operation, therefore nitrogen not used. Solvent flow started at 10:52.

BENCH SCALE EXTRACTOR
DATA SHEET

RUN # 3
DATE 9/8/82
DESCRIPTION Bromacil Wastewater

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	3:30	100	7	1650		4740	40			0.51
T_0	4:00	100	7	1635	20	4740	40	1200	2:1	0.76
T_1	4:30	100	7	1615	20	5340	40	2400	2:1	0.76
T_2	5:00	100	6	1595	20	5940	40	3600	2:1	0.76
T_3	5:30	100	6	1590	20	6540	40	4800	2:1	0.76
T_4	6:00	100	6	1585	20	7140	40	6000	2:1	0.76
T_5	6:30	100	6	1580	20	7740	40	7200	2:1	0.76

COMMENTS: Bromacil plant wastewater dispersed in hexane. Solvent recovery system in operation and returning solvent to the extractor.

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 4
DATE 11/18/82
DESCRIPTION Bromacil Wastewater

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	10:50	100	7.5	1575		4740	40			0.51
T_0	11:20	100	7.5	1550		4740	40	1200		0.51
T_1	11:50	100	7.5	1525	20	4940	40	2400	2:1	0.76
T_2	12:20	100	7.5	1505	20	5540	40	3600	2:1	0.76
T_3	12:50	100	7.5	1480	20	6140	40	4800	2:1	0.76
T_4	1:20	100	7.5	1455	20	6740	40	6000	2:1	0.76
T_5	1:50	100	7.5	1430	20	7340	40	7200	2:1	0.76

COMMENTS: Bromacil plant wastewater dispersed in butyl chloride. Solvent recovery system in operation but not returning solvent to the extractor. Solvent flow started 11:40.

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 5
DATE 12/3/82
DESCRIPTION Bromacil Wastewater

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	10:55	100	5	1130		4740	40			0.51
T_0	11:25	100	5	1125		4740	40	1200		0.51
T_1	11:55	100	5	1120	20	5040	40	2400	2:1	0.76
T_2	12:25	100	5	1115	20	5640	40	3600	2:1	0.76
T_3	12:55	100	5	1110	20	6240	40	4800	2:1	0.76
T_4	1:25	100	5	1105	20	6840	40	6000	2:1	0.76
T_5	1:55	100	5	1100	20	7440	40	7200	2:1	0.76

COMMENTS: Duplicate of Run 4, bromacil plant wastewater dispersed in butyl chloride. Solvent flow started at 11:40.

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 6
DATE 1/21/83
DESCRIPTION 2,4-D Wastewater

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	9:57	100	8	1075		4740	40			0.51
T_0	10:57	100			20	5140	40	2400	2:1	0.76
T_1	11:27	100			20	5740	40	3600	2:1	0.76
T_2	11:57	100			20	6340	40	4800	2:1	0.76
T_3	12:27	100			20	6940	40	6000	2:1	0.76
T_4										

COMMENTS: 2,4-D plant wastewater dispersed in butyl chloride. Use of solvent recovery system terminated at 10:10. Solvent flow started at 10:37. Run stopped at 12:27 due to uncontrollable leak in water flow meter. Sample T_4 taken from treated water remaining in extractor column.

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 7
DATE 2/24/83
DESCRIPTION 2,4-D Wastewater

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	10:12	100	7	575		4740	80			1.01
T_0	10:42	100	7	550	20	4980	80	2400	4:1	1.27
T_1	11:12	100	7	525	20	5580	80	4800	4:1	1.27
T_2	11:42	100	7	500	20	6180	80	7200	4:1	1.27
T_3	12:12	100	7	490	20	6780	80	9600	4:1	1.27
T_4	12:42	100	7	470	20	7380	80	12000	4:1	1.27
T_5	1:12	100	7	450	20	7980	80	14400	4:1	1.27

COMMENTS: 2,4-D plant wastewater dispersed in butyl chloride. Water flow rate doubled from previous runs to 80 ml/min. Solvent flow started at 10:30. Water/solvent volume ratio in extractor column not controlled properly changing from approximate ratios of 1:4 to 4:1 over the course of the run. Solvent recovery system disconnected at 11:30, but nitrogen flow allowed to continue in order to clear the overloaded stripper.

BENCH SCALE EXTRACTOR DATA SHEET

RUN # 8
DATE 3/4/83
DESCRIPTION 2,4-D Wastewater

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
S	9:45	100	6	450		4740	80			1.01
T_0	10:15	100	6	445	20	5040	80	2400	4:1	1.27
T_1	10:45	100	6	440	20	5640	80	4800	4:1	1.27
T_2	11:15	100	6	430	20	6240	80	7200	4:1	1.27
T_3	11:45	100	6	425	20	6840	80	9600	4:1	1.27
T_4	12:15	100	6	420	20	7440	80	12000	4:1	1.27
T_5	12:45	100	6	420	20	8040	80	14400	4:1	1.27
T_6	1:15	100	6	415	20	8640	80	16800	4:1	1.27

COMMENTS: 2,4-D plant wastewater dispersed in butyl chloride. Seven-hour run. Solvent flow started at 10:00. Solvent recovery system disconnected at 10:45, but nitrogen flow continued until 3:30.

BENCH SCALE EXTRACTOR
DATA SHEET

RUN # 8
DATE 3/4/83
DESCRIPTION 2,4-D Wastewater

SAMPLE	TIME	MOTOR SPEED	NITROGEN		SOLVENT		WATER		RATIO	EXCHANGES PER HOUR
			PSI IN	TANK PSI	FLOW RATE ml/min	VOLUME ml	FLOW RATE ml/min	VOLUME ml	WATER/ SOLVENT	
T_7	1:45	100	6	410	20	9240	80	19200	4:1	1.27
T_8	2:15	100	6	405	20	9840	80	21600	4:1	1.27
T_9	2:45	100	8	400	20	10440	80	24000	4:1	1.27
T_{10}	3:15	100	8	380	20	11040	80	26400	4:1	1.27
T_{11}	3:45	100			20	11640	80	28800	4:1	1.27
T_{12}	4:15	100			20	12240	80	31200	4:1	1.27
T_{13}	4:45	100			20	12840	80	33600	4:1	1.27

APPENDIX B

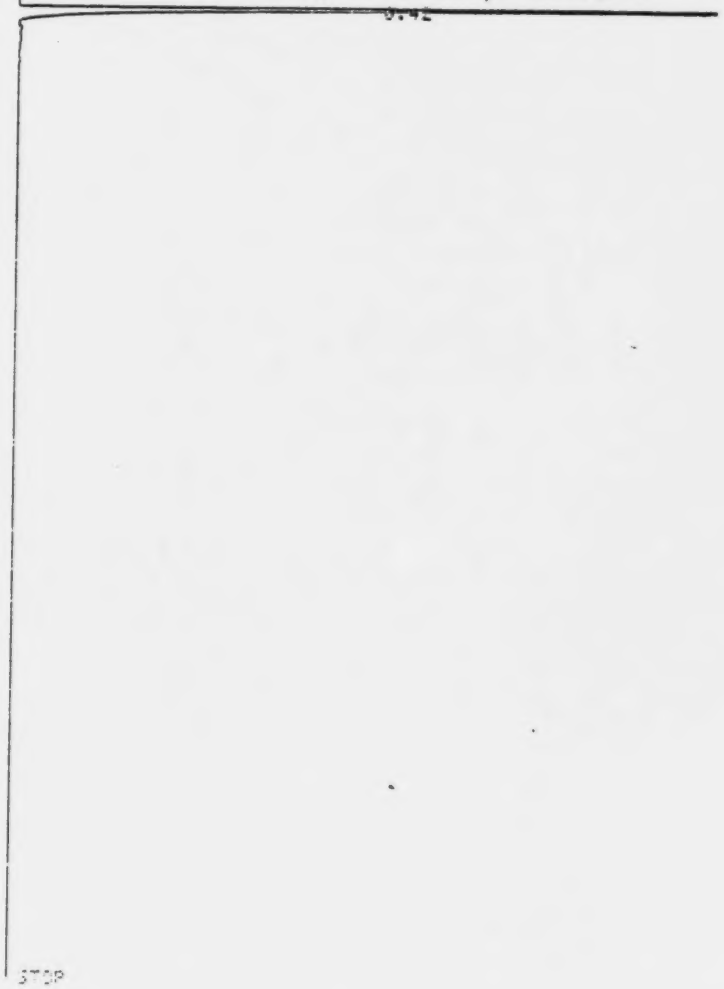
GAS CHROMATOGRAPHIC DATA FOR RUNS 1 THOUGH 8

The following chromatograms were generated by a Varian Model 3700 Gas Chromatograph with a pesticide column, 6-ft long x 2-mm ID, packed with 1.5 percent SP-2250/1.95 percent SP-2401 on 100/120 Supelcoport.

Run 1, the field blank, is represented by one chromatogram which consists of a composite of solvent aliquots T_0 through T_5. This chromatogram indicates that the RDC system was free of contaminants.

For bromacil (Runs 2-5), GC peak retention times vary from run to run, spanning the range of 4.55 to 5.01 minutes. Chromatograms for 2,4-D (Runs 6-8) show several peaks, although only one is representative. Retention times for this peak fall in the range of 2.54 to 2.68 minutes. Calibration standards run with each set of samples eliminated any question regarding correct retention times or representative peaks. Calibration standards for Run 2 may be viewed in Appendix D.

START 00.00.00.00. RUN 1 Blank because dissolved in water
Composite of solvent aliquots T₀ through T₆



RUN 1
Field Blank

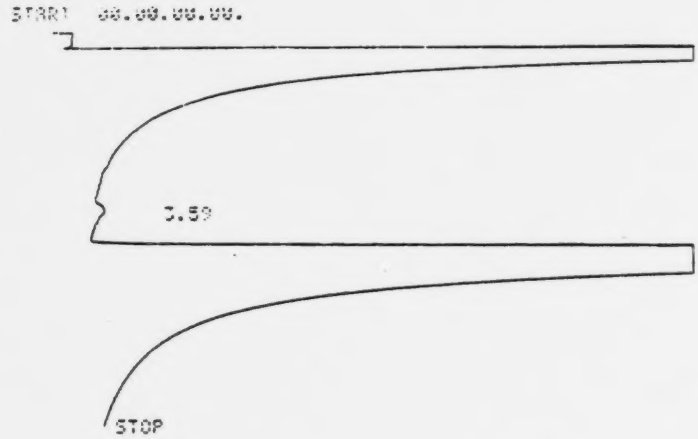
STOP

C-R1A
SMPL # 40
FILE # 3
REPT # 1510
METHOD -1

#	NAME	TIME	CONC	MK	AREA
0		0.42	99.9999		6241
	TOTAL		99.9999		6241

Reproduced from best available copy.

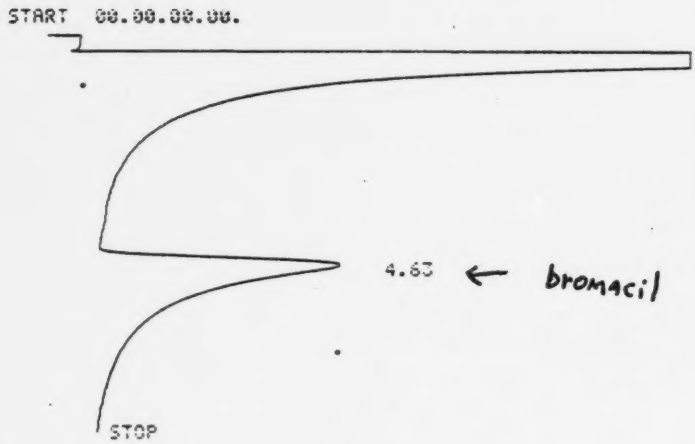
Run 2
Starting Material



C-RIA
SMPL # 00
FILE # 1
REPT # 2454
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		3.59	0.0000		222
		4.63			103137
	TOTAL		0.0000		103360

Run 2
To

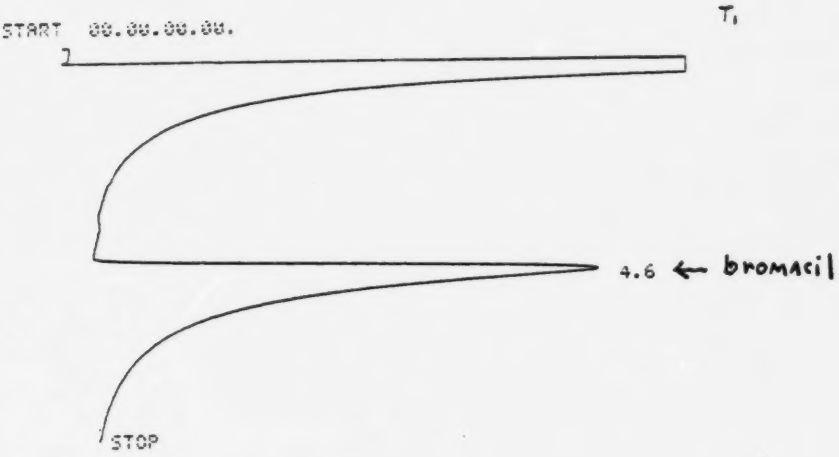


C-RIA
SMPL # 00
FILE # 1
REPT # 2436
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.63			19920
	TOTAL		0		19920

Reproduced from best available copy.

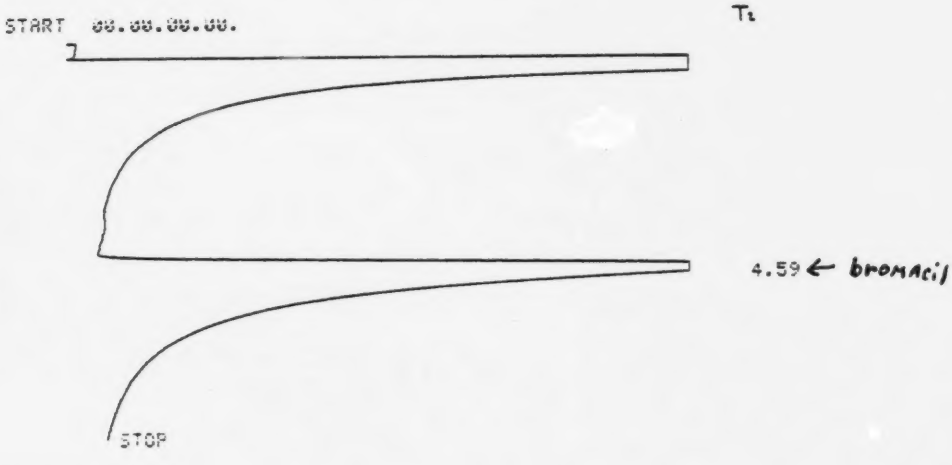
Run 2
T_1



C-RIA
SMPL # 00
FILE # 1
REPT # 2440
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.6			39536
	TOTAL		0		39536

Run 2
T_2

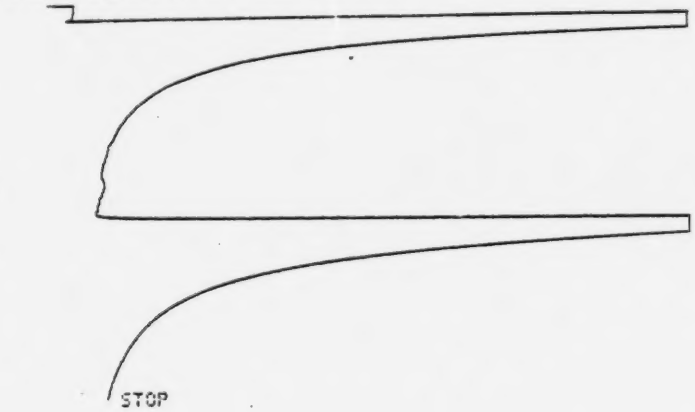


C-RIA
SMPL # 00
FILE # 1
REPT # 2444
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.59			50961
	TOTAL		0		50961

Run 2
T3

START 00.00.00.00.



4.59 ← bromacil

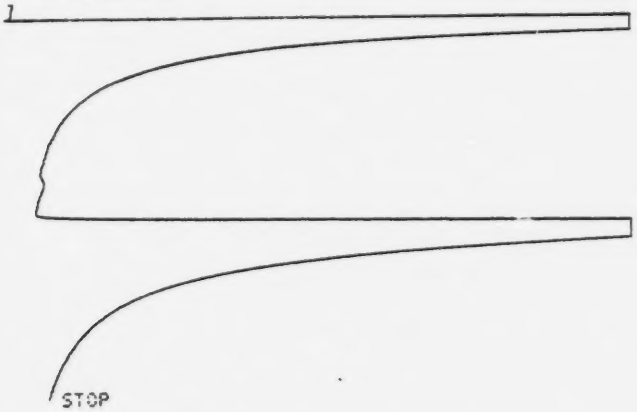
STOP

C-R1A
SMPL # 00
FILE # 1
REPT # 2444
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.59			61159
	TOTAL		0		61159

Run 2
T4

START 00.00.00.00.

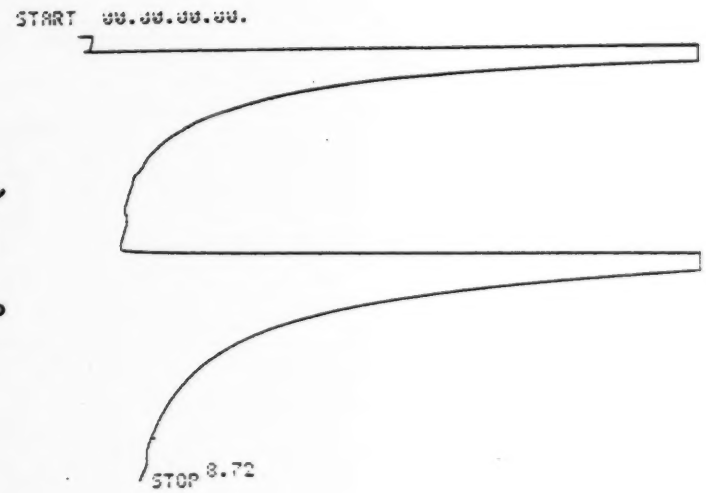


4.59 ← bromacil

STOP

C-R1A
SMPL # 00
FILE # 1
REPT # 2446
METHOD 44

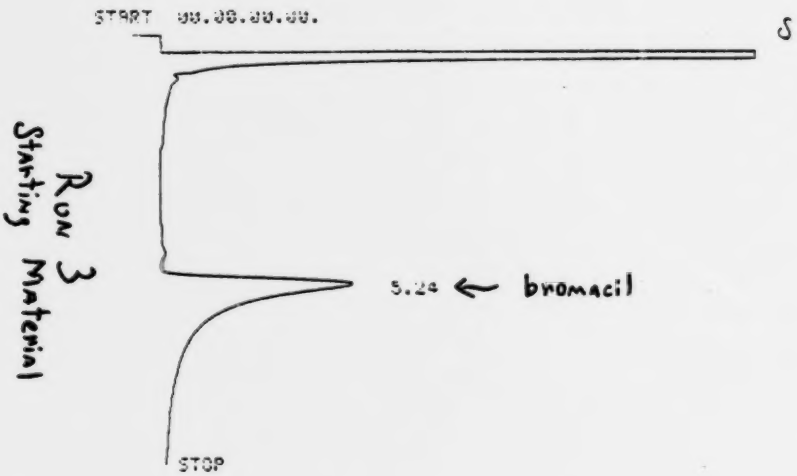
#	NAME	TIME	CONC	MK	AREA
		4.59			65300
	TOTAL		0		65300



Run T5 2

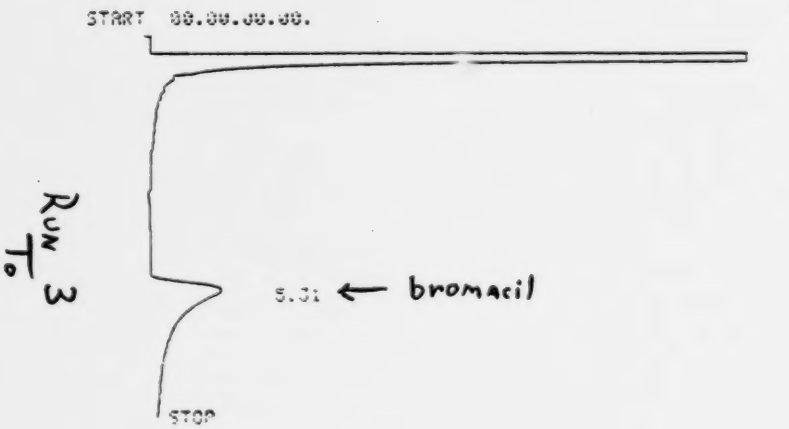
C-R1A
SMPL # 00
FILE # 1
REPT # 2525
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.68	0.9109		71967
		8.72	0.0021	:	57
		TOTAL	0.921		72024



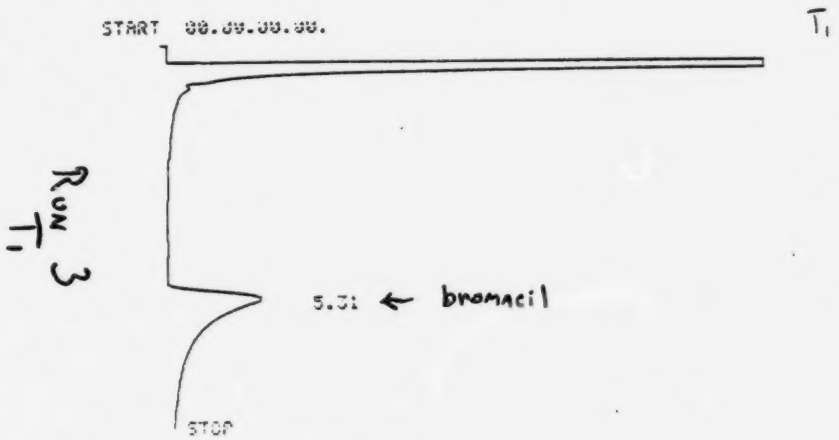
C-R1A
SMPL # 00
FILE # 1
REPT # 2643
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		5.24			12879
	TOTAL		0		12879



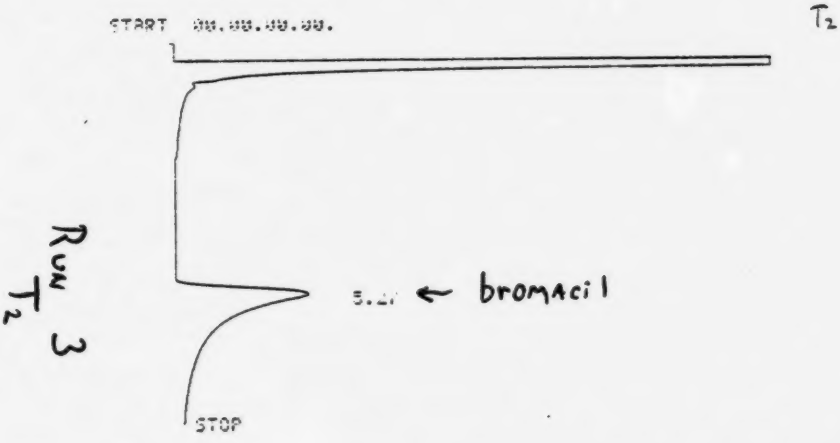
C-R1A
SMPL # 00
FILE # 1
REPT # 2644
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		5.31			5383
	TOTAL		0		5383



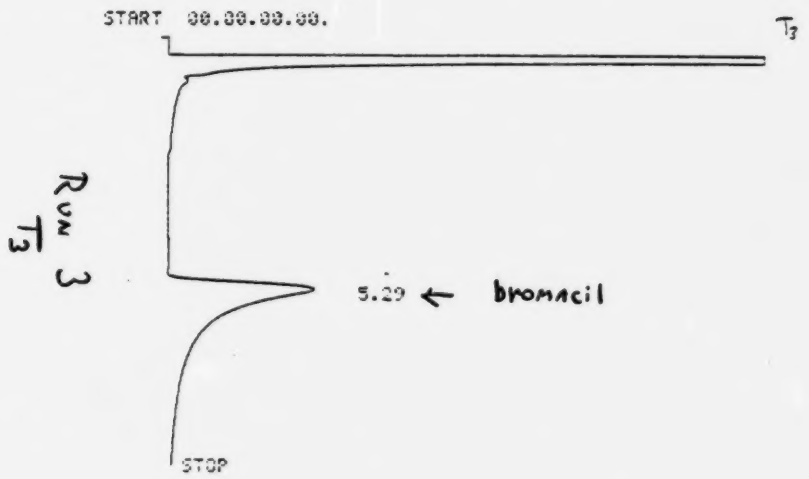
C-RIA
SMPL # 00
FILE # 1
REPT # 2632
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		5.31			7050
	TOTAL		0		7050



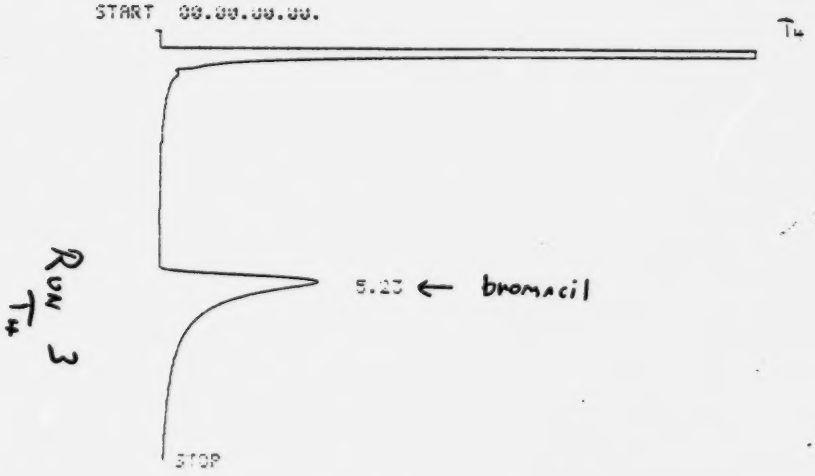
C-RIA
SMPL # 00
FILE # 1
REPT # 2633
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		5.27			9554
	TOTAL		0		9554



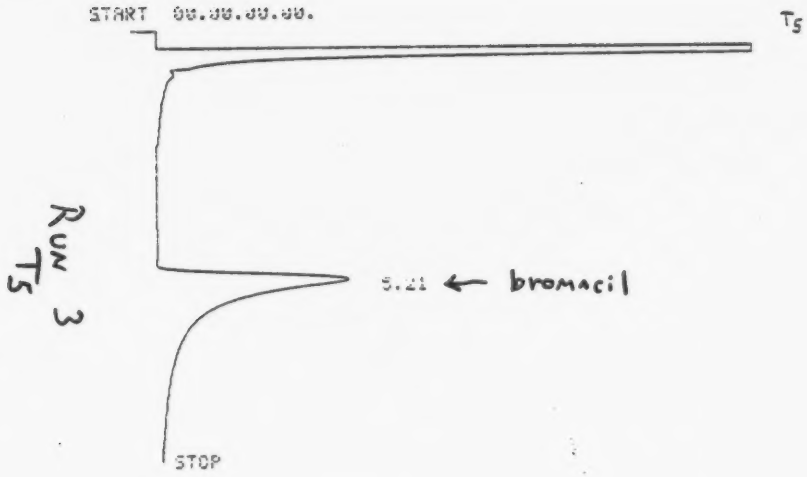
C-RIA
SMPL # 00
FILE # 1
REPT # 2640
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		5.29			10794
	TOTAL		0		10794



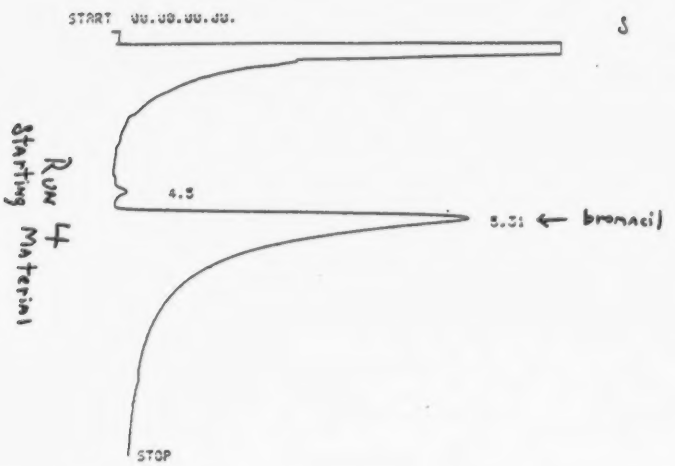
C-RIA
SMPL # 44
FILE # 1
REPT # 2641
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		5.23			10923
	TOTAL		0		10923



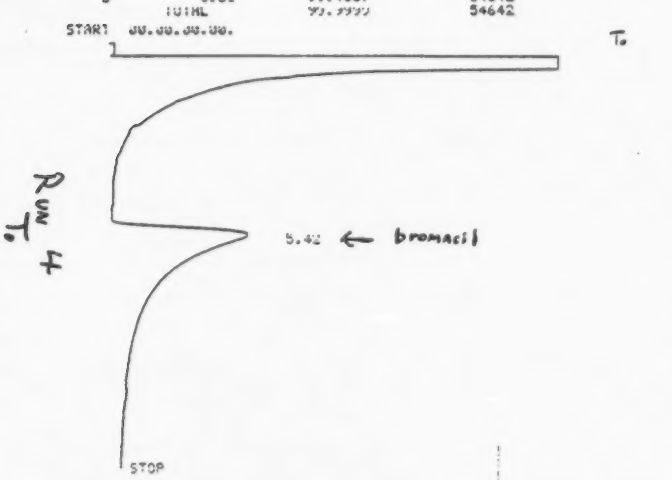
C-18A
SMPL # 00
FILE # 1
REPT # 2842
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		5.21	0.1184		12834
		0 ML	0.1184		12834



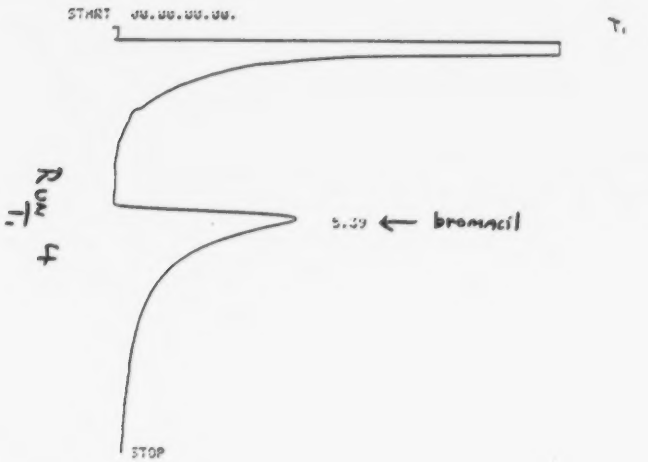
SCALIM
SMPL # 00
RUN # 1
REPT # 200
METHOD 41

#	NAME	TIME	CONC	RK	AREA
B		4.8	0.5432		788
B		5.31	99.4567		54742
	TOTAL		99.9999		54642



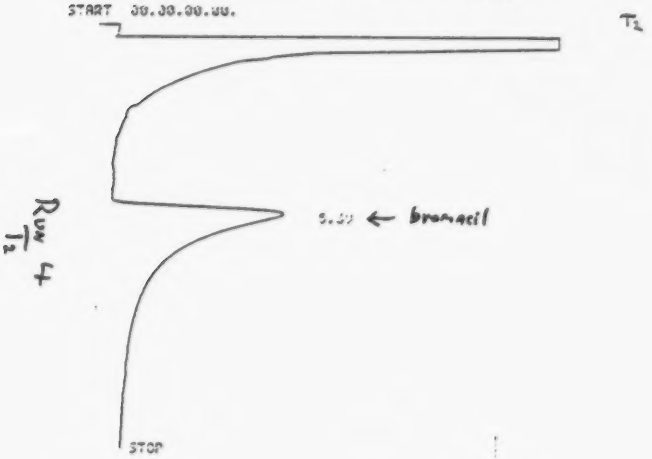
SCALIB
SMPL # 00
RUN # 1
REPT # 200
METHOD 41

#	NAME	TIME	CONC	RK	AREA
B		5.42	99.9999		55472
	TOTAL		99.9999		55472



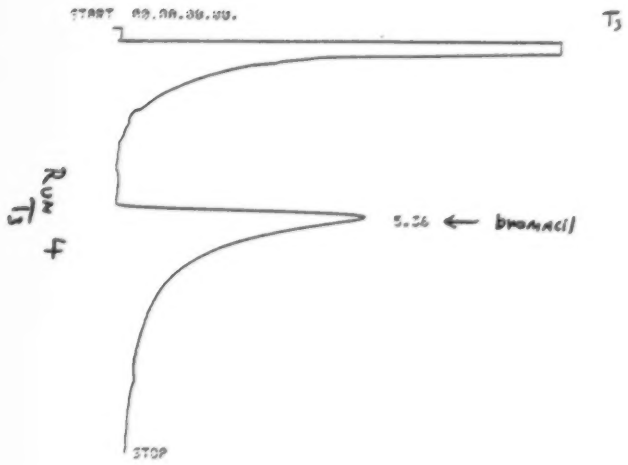
C-21A
SMPL # 00
FILE # 1
RCPT # 243
METHOD 41

#	NAME	TIME	QUAL	TX	AREA
8		5.39	99.9999		29502
	TOTAL		99.9999		29502



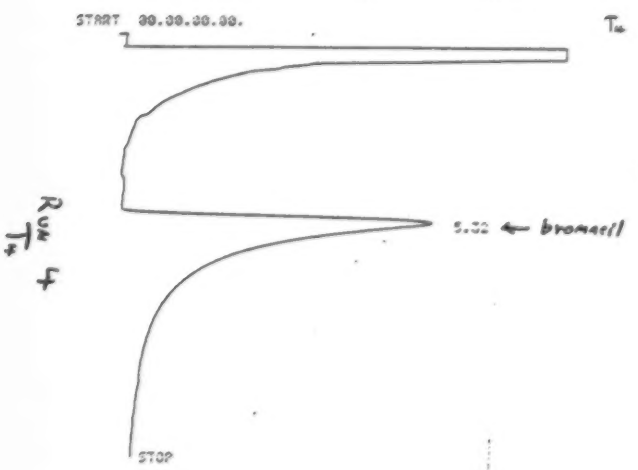
C-21A
SMPL # 00
FILE # 1
RCPT # 244
METHOD 41

#	NAME	TIME	QUAL	TX	AREA
8		5.39	99.9999		28764
	TOTAL		99.9999		28764



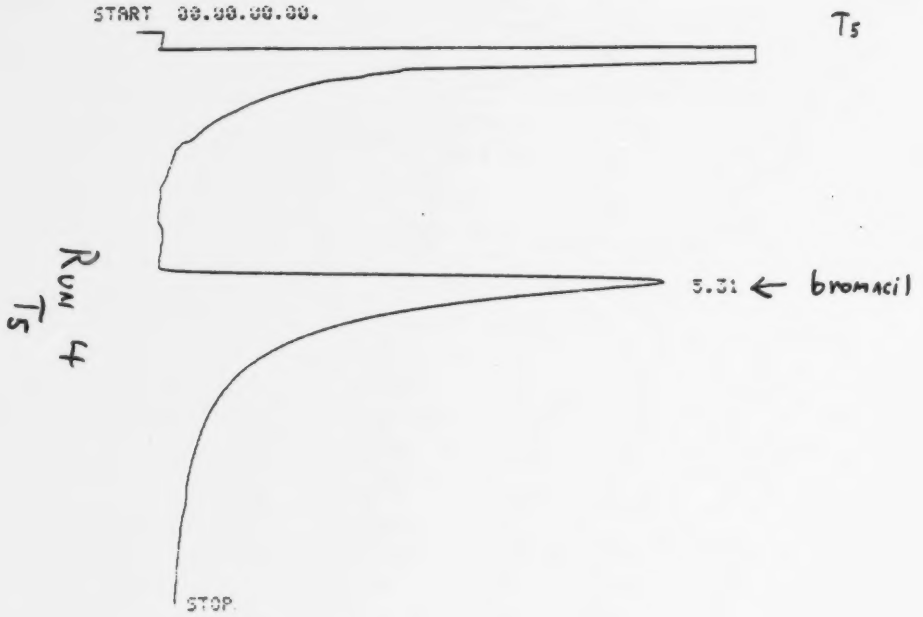
C-21A
SMPL # 40
FILE # 1
REPT # 242
METHOD 41

#	NAME	TIME	CONC	RK	AREA
3		5.36	??.????		38818
	TOTAL		??.????		38818



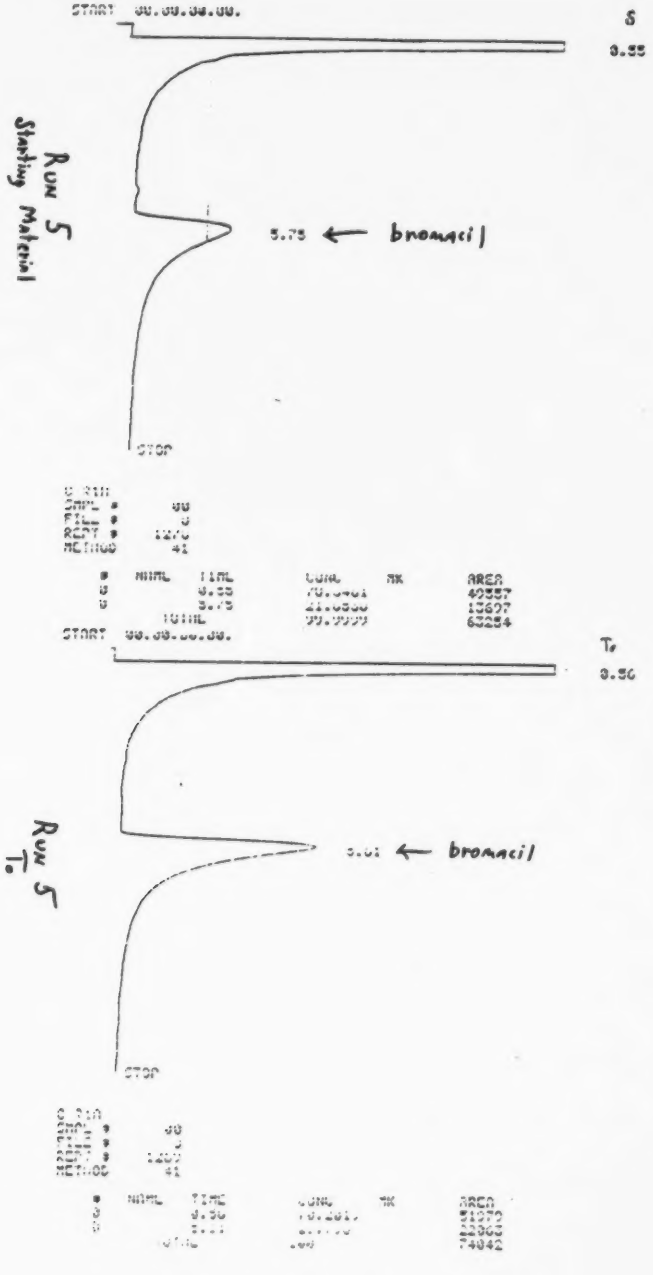
C-21A
SMPL # 40
FILE # 1
REPT # 244
METHOD 41

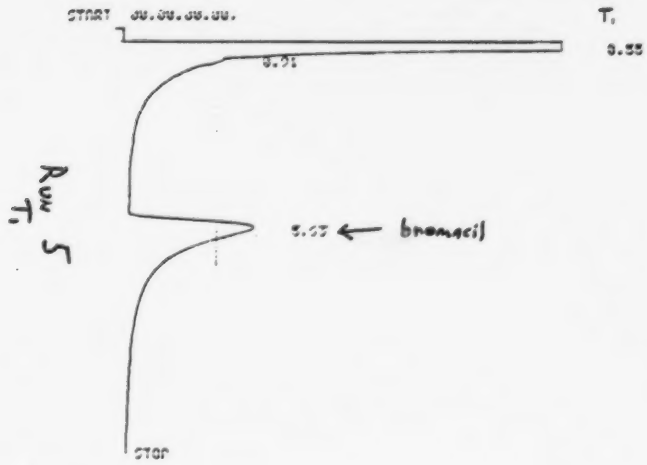
#	NAME	TIME	CONC	RK	AREA
3		5.32	??.????		44092
	TOTAL		??.????		44092



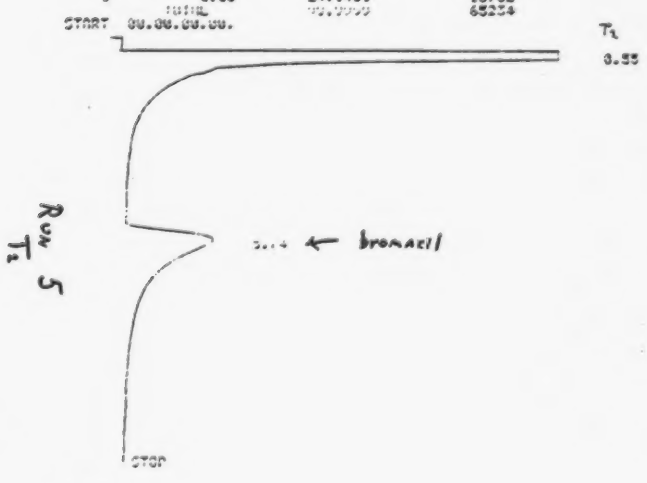
C-RIM
SMPL # 00
FILL # 1
REPT # 400
METHOD 71

#	NAME	TIME	CONC	MK	AREA
8		5.31	99.9999		53832
	TOTAL		99.9999		53832

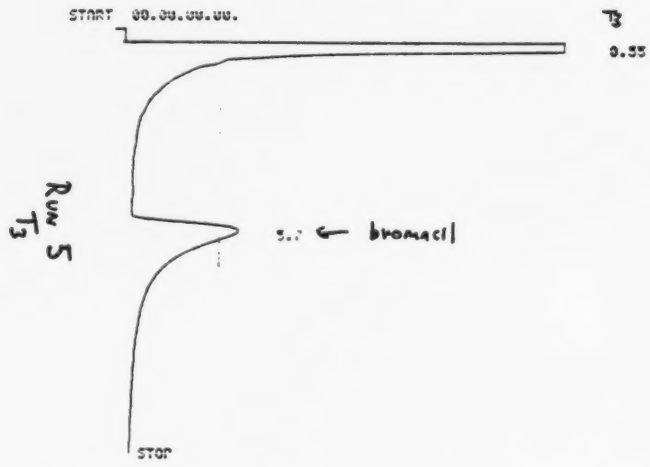

START 00.00.00.00.
5
0.55
Run 5
Starting Material
5.75 ← bromacil
STOP
NAME TIME AREA
1 0.55 40557
2 5.75 13607
TOTAL 63284
START 00.00.00.00.
T₀
0.56
Run 5
T₀
5.61 ← bromacil
STOP
NAME TIME AREA
1 0.56 41070
2 5.61 22908
TOTAL 74042



#	NAME	TIME	CONC	RK	AREA
0		0.55	75.7120		40331
0		0.91	0.1000		20
0		1.00	24.1401		15752
	TOTAL		99.9759		65324

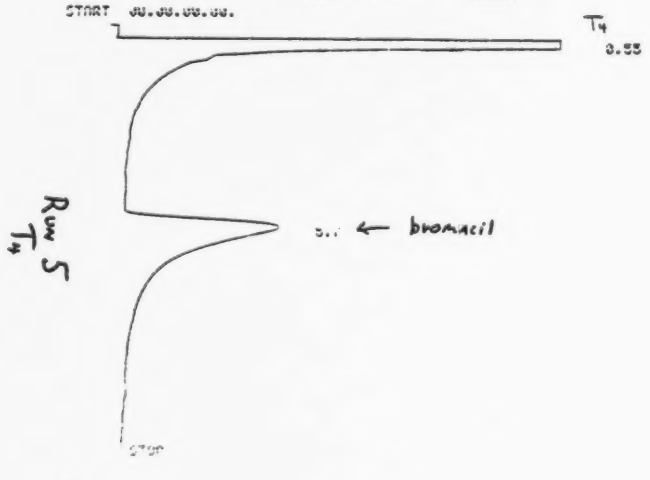


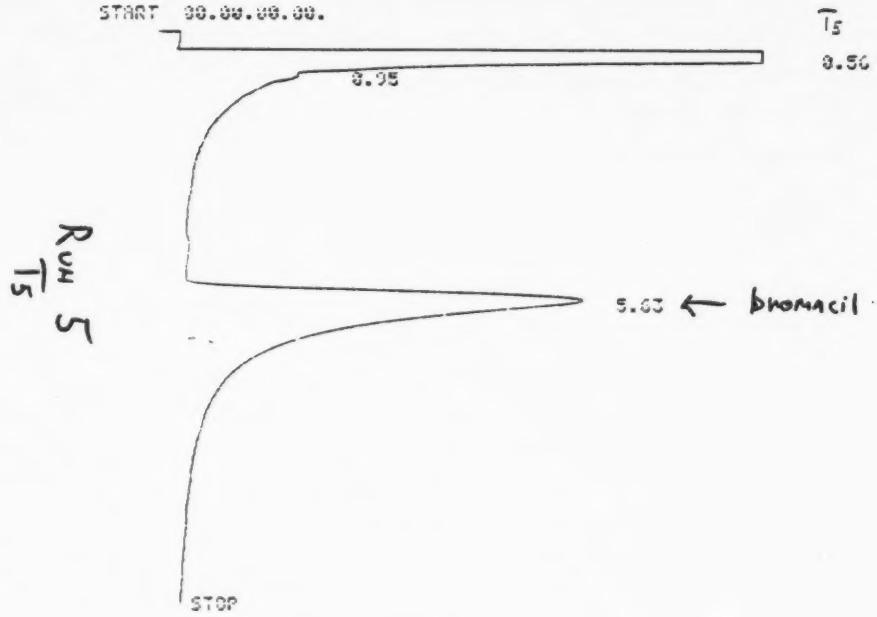
#	NAME	TIME	CONC	RK	AREA
0		0.55	00.7510		40316
0		0.74	[illegible]		11255
	TOTAL		[illegible]		08572



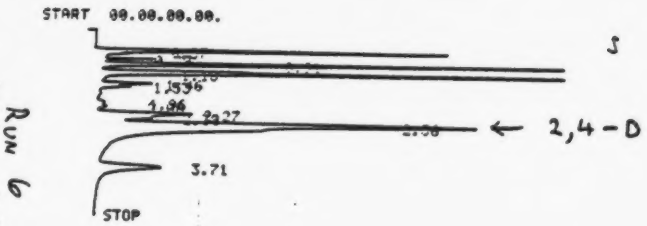
C:\RIA
SMPL # 68
FILE # 0
RCPT # 1273
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.55	77.0565		50003
0		5.7	22.9434		14411
	TOTAL		99.9999		64501





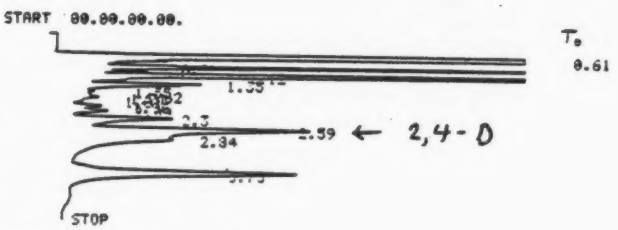

```
C RUN
SMPL #      60
FILL #       0
RCPT #    1475
METHOD      41

   #   AMML     TIME        CONC      MK      AREA
   0           0.50        0.0000            40000
   0           0.95        0.1100  ,            95
   0           5.00       41.0515            35340
           TOTAL          0.0000            84443
```



Run 6 Starting Material

C-R1A
SMPL # 00
FILE # 8
REPT # 1782
METHOD 41

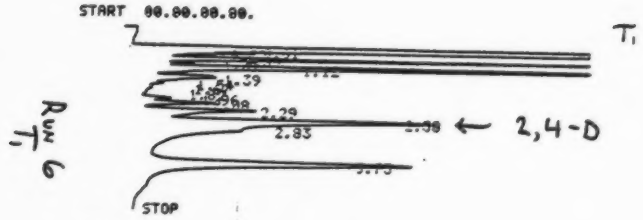
#	NAME	TIME	CONC	MK	AREA
0		0.57	10.09		2300
0		0.79	1.7528	V	399
0		0.91	14.304	V	3260
0		1.18	18.362	V	4186
0		1.46	1.7131	V	390
0		1.53	1.0278	V	234
0		1.96	0.3579		81
0		2.06	0.3878	V	88
0		2.27	5.16		1176
0		2.38	2.8006	V	638
0		2.56	38.2337	V	8716
0		3.71	5.8078		1324
	TOTAL		100		22797



Run T₀ 6

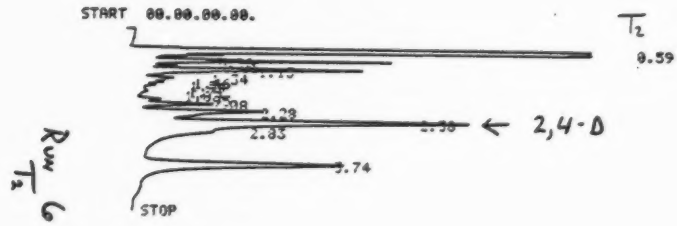
C-R1A
SMPL # 00
FILE # 8
REPT # 1692
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.61	33.8453		19368
0		0.9	11.7209	V	6707
0		1.01	1.2863	V	736
0		1.12	17.103	V	9787
0		1.35	3.7859	V	2166
0		1.55	0.5461	V	312
0		1.62	0.568	V	325
0		1.71	0.7587	V	434
0		1.81	0.4679	V	267
0		1.96	0.8712	V	498
0		2.09	1.14	V	652
0		2.3	3.6548	V	2091
0		2.59	9.4872	V	5383
0		2.84	5.5573	V	3180
0		3.75	9.2867	V	5314
	TOTAL		99.9999		57225



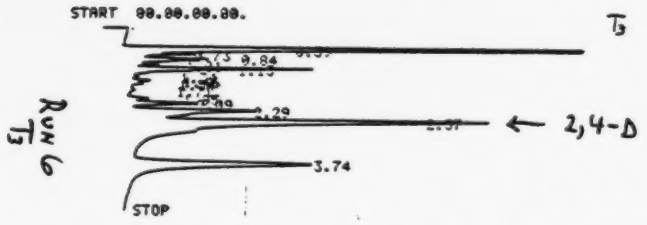
C-R1A
SMPL # 90
FILE # 9
REPT # 1693
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.61	34.4629		19173
0		0.72	1.7853	V	993
0		0.89	6.708	V	3732
0		1.01	0.9558	V	531
0		1.12	11.5642	V	6433
0		1.39	2.7015	V	1503
0		1.54	0.5744	V	319
0		1.67	0.6052	V	336
0		1.82	0.3528	V	196
0		1.96	0.8227	V	457
0		2.08	1.7973	V	999
0		2.29	4.3907	V	2442
0		2.58	12.6802	V	7010
0		2.83	6.824	V	3796
0		3.75	13.854	V	7707
	TOTAL		99.9999		55635



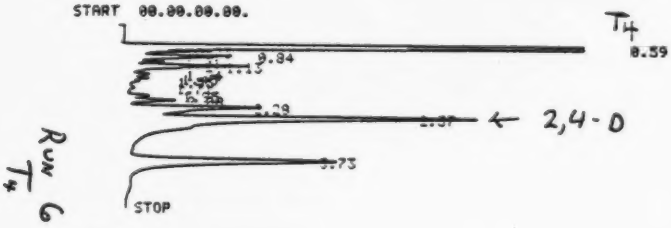
C-R1A
SMPL # 90
FILE # 9
REPT # 1694
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.59	43.7153		17220
0		0.89	5.1298	V	2020
0		1.01	0.8702	V	342
0		1.13	6.795	V	2676
0		1.34	1.2179	V	479
0		1.46	0.5438	V	214
0		1.54	0.4672	V	184
0		1.71	0.4876	V	192
0		1.83	0.0676	V	26
0		1.95	0.5706	V	224
0		2.08	1.9794	V	779
0		2.29	5.8769	V	2315
0		2.58	17.1233	V	6745
0		2.83	4.284	V	1687
0		3.74	10.8707		4282
	TOTAL		99.9999		39391



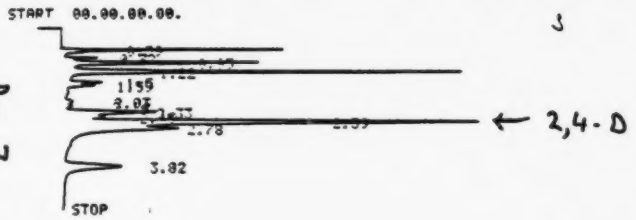
C-R1A
SMPL # 00
FILE # 8
REPT # 1695
METHOD 41

#	NAME	TIME	CONC	MX	AREA
0		0.59	38.2517		11640
0		0.73	0.4651	T	141
0		0.84	2.0058	T	610
0		1.01	0.3081	TV	93
A		1.13	6.2615	V	1905
0		1.34	0.1097	T	33
0		1.46	0.5755	V	175
0		1.54	0.4694	V	142
0		1.71	0.3136	V	95
0		1.95	0.5879	V	178
0		2.09	2.2534	V	685
0		2.29	7.6284	V	2321
0		2.57	27.7986	V	8459
0		3.74	12.9707		3947
	TOTAL		99.9999		30432



C-R1A
SMPL # 00
FILE # 8
REPT # 1697
METHOD 41

#	NAME	TIME	CONC	MX	AREA
0		0.59	46.1249		16401
0		0.73	0.4513	T	160
0		0.84	2.2747	T	808
0		1.01	0.3347	TV	119
0		1.13	4.2282	V	1503
0		1.34	0.7499	V	266
A		1.45	0.5066	V	180
0		1.53	0.3603	V	128
0		1.71	0.3832	V	136
0		1.95	0.6711	V	238
0		2.08	1.3874	V	493
0		2.29	6.6811	V	2375
0		2.57	23.3252	V	8294
0		3.73	12.5208		4452
	TOTAL		99.9999		35858

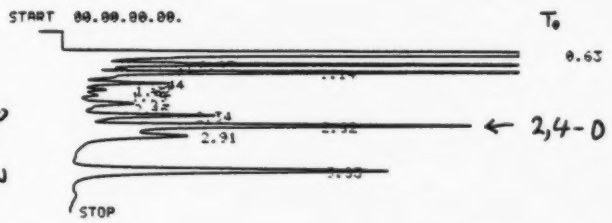


Run 7
Starting Material

3

C-R1A
SMPL # 00
FILE # 8
REPT # 1939
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.59	6.4868		1086
0		0.82	1.1662	V	197
0		0.95	10.468	V	1774
0		1.22	18.4233	V	3123
0		1.5	1.793	V	303
0		1.59	1.3191	V	223
0		2.03	0.49		83
0		2.14	0.3633	V	61
0		2.33	6.4925		1100
0		2.45	2.378	V	403
0		2.59	32.6263	V	5531
0		2.78	11.4889	V	1947
0		3.82	6.584		1116
	TOTAL		99.9999		16954

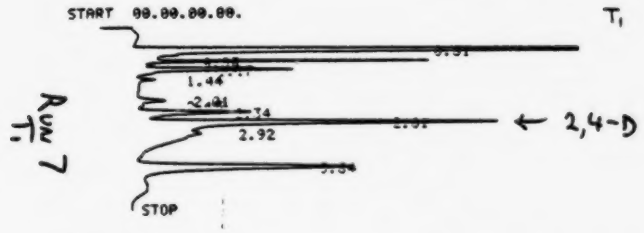


Run 7
T₀

T₀

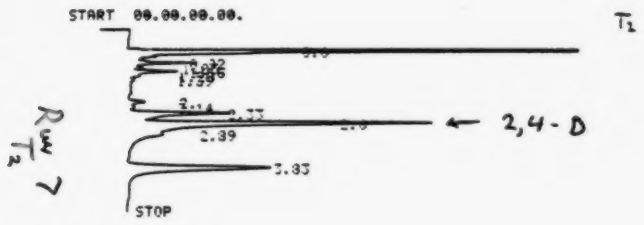
C-R1A
SMPL # 00
FILE # 9
REPT # 1928
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.63	37.987		21523
0		0.93	13.2899	V	7530
0		1.04	1.0252	V	580
0		1.14	10.5898	V	6000
0		1.44	2.3797	V	1347
0		1.62	0.8337	V	472
0		1.76	0.8561	V	485
0		2.	2.1607	V	1224
0		2.13	0.5045	V	285
0		2.34	4.2065	V	2383
0		2.62	10.746	V	6088
0		2.91	4.8616	V	2754
0		3.85	10.5596		5983
	TOTAL		99.9999		56660



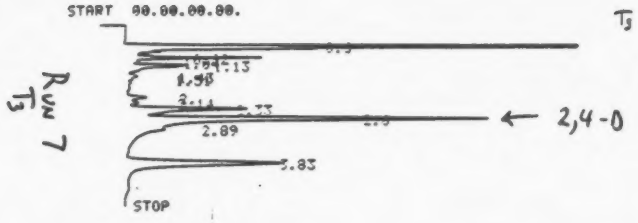
C-R1A
SMPL # 00
FILE # 3
REPT # 1929
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.61	41.3533		12885
0		0.93	5.3026	V	1652
0		1.05	0.403	V	125
0		1.17	5.7328	V	1786
0		1.44	0.4177	V	130
0		2.01	1.048		326
0		2.15	0.24	V	74
0		2.34	4.9752	V	1550
0		2.61	18.4855	V	5759
0		2.92	9.2784	V	2889
0		3.84	12.771		3979
	TOTAL		99.9999		31159



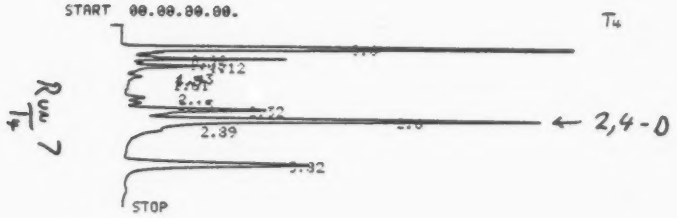
C-R1A
SMPL # 00
FILE # 3
REPT # 1931
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.6	44.468		9202
0		0.92	2.6266	V	543
0		1.05	0.5939	V	122
0		1.16	2.2819	V	472
0		1.29	0.4302	V	89
0		1.39	0.1982	V	41
0		2.	0.8122		168
0		2.14	0.3691	V	76
0		2.33	7.4046	V	1532
0		2.6	23.4721	V	4857
0		2.89	3.7745	V	781
0		3.83	15.3682		2907
	TOTAL		100.		20693



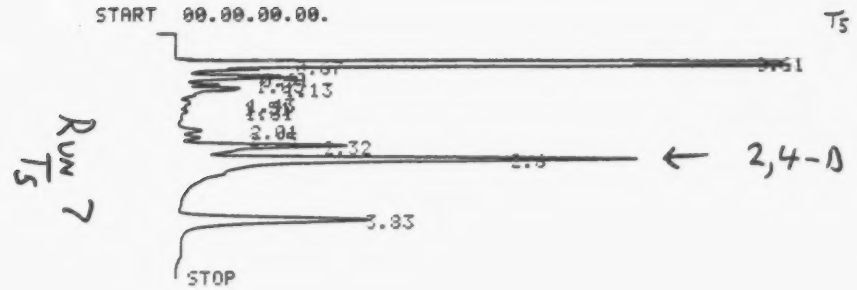
C-91A
SMPL # 00
FILE # 8
REPT # 1932
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.6	43.1818		10333
0		0.92	3.9802	V	952
0		1.04	0.4437	V	106
0		1.13	3.3189	V	794
0		1.43	0.4127	V	98
0		1.51	0.093	V	22
0		2.	0.7918		189
0		2.14	0.4659	V	111
0		2.33	7.4831	V	1790
0		2.6	23.4261	V	5605
0		2.89	4.0071	V	958
0		3.83	12.3953		2966
	TOTAL		99.9999		23929



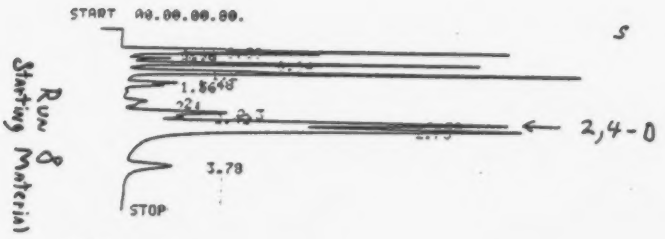
C-91A
SMPL # 98
FILE # 9
REPT # 1934
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.6	40.0694		10469
0		0.92	4.3089	V	1125
0		1.05	0.5581	V	145
0		1.12	3.5508	V	927
0		1.43	0.6334	V	165
0		1.5	0.1156	V	30
0		1.61	0.0725	V	18
0		2.	0.7846		205
0		2.15	0.6275	V	163
0		2.32	8.2105	V	2145
0		2.6	27.2054	V	7108
0		2.89	0.2588	T	52
0		3.82	12.6239		3359
	TOTAL		100		26127



C-R1A
SMPL # 00
FILE # 8
REPT # 1935
METHOD 41

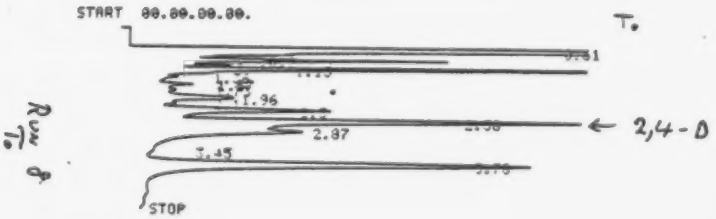
#	NAME	TIME	CONC	MK	AREA
0		0.61	34.2678		9786
0		0.67	19.4556	V	5556
0		0.91	3.2794	V	936
0		1.05	0.7441	V	212
0		1.13	2.3778	V	679
0		1.43	0.3815	V	108
0		1.51	0.1263	V	36
0		1.61	0.1891	V	54
0		2.01	0.6344		181
0		2.15	0.5421	V	154
0		2.32	6.7587	V	1930
0		2.6	21.7371	V	6208
0		3.83	9.5055		2714
	TOTAL		99.9999		28560



Run 8 Starting Material

C-R1A
SMPL # 00
FILE # 8
REPT # 2159
METHOD 41

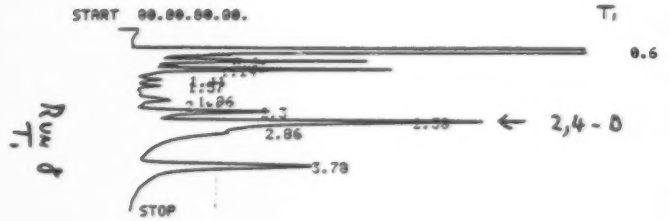
#	NAME	TIME	CONC	MK	AREA
0		0.59	0.7776		2512
0		0.66	2.743	V	785
0		0.74	0.3305	V	94
0		0.8	1.1395	V	326
0		0.94	8.871	V	2538
0		1.2	14.0309	V	4015
0		1.48	1.4884	V	400
0		1.56	1.1683	V	334
0		2.	1.0022		286
0		2.1	0.3293	V	94
0		2.3	4.7775	V	1367
0		2.42	2.3738	V	679
0		2.58	19.6462	V	5622
0		2.75	29.4073	V	8416
0		3.78	4.0018	V	1145
	TOTAL		99.9999		28618



Run 8 T.

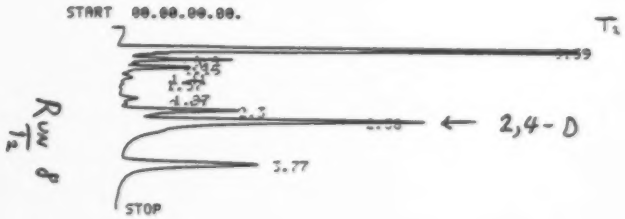
C-R1A
SMPL # 00
FILE # 8
REPT # 2139
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.61	30.4816		18418
0		0.9	4.9474	V	2989
0		1.03	1.4819	V	895
0		1.15	18.3247	V	11072
0		1.36	0.1453	T	87
0		1.57	0.5046	T	304
0		1.73	0.2767	TV	167
0		1.96	2.0659	TV	1248
0		2.1	0.1755	TV	105
0		2.3	6.1962	V	3744
0		2.58	14.1622	V	8557
0		2.87	7.4259	V	4487
0		3.45	0.3104	V	187
0		3.78	12.5812	V	8158
	TOTAL		100		60426



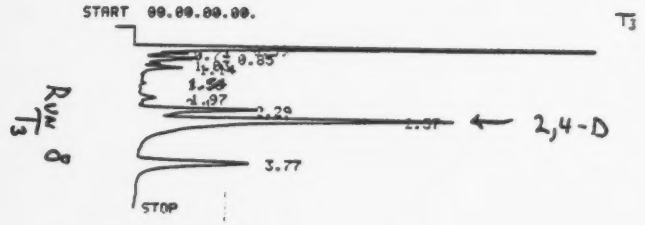
C-R1A
SMPL # 90
FILE # 8
REPT # 2140
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.6	44.1232		17501
0		0.9	4.908	V	1946
0		1.03	0.7788	V	309
0		1.14	5.9286	V	2351
0		1.41	0.6296	V	249
0		1.57	0.4146	V	164
0		1.96	1.1007		436
0		2.11	0.0842	V	33
0		2.3	5.2764		2092
0		2.58	17.9257	V	7109
0		2.86	7.847	V	3112
0		3.78	10.9806	V	4355
	TOTAL		99.9999		39662



C-R1A
SMPL # 90
FILE # 8
REPT # 2141
METHOD 41

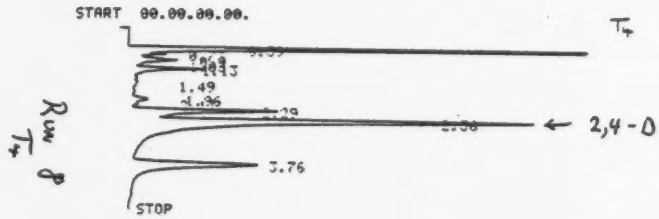
#	NAME	TIME	CONC	MK	AREA
0		0.59	46.038		12360
0		0.9	3.7337	V	1002
0		1.02	0.493	V	132
0		1.13	3.3688	V	904
0		1.41	0.6869	V	184
0		1.57	0.1072	V	28
0		1.97	0.7537		202
0		2.12	0.225	V	60
0		2.3	7.0193	V	1884
0		2.58	25.9879	V	6977
0		3.77	11.5869		3110
	TOTAL		100		26840



Run of T3

C-R1A
SMPL # 00
FILE # 8
REPT # 2143
METHOD 41

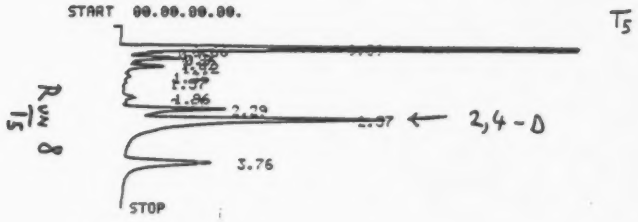
#	NAME	TIME	CONC	MK	AREA
0		0.59	41.9783		9296
0		0.74	0.552	T	122
0		0.85	2.3614	T	522
0		1.03	0.4006	TV	88
0		1.14	1.7899	TV	396
0		1.34	0.2402	T	53
0		1.56	0.1774	TV	39
0		1.97	0.8578		189
0		2.1	0.1532	V	33
0		2.29	8.8348		1956
0		2.57	31.3601	V	6944
0		3.77	11.2937		2501
	TOTAL		99.9999		22145



Run of T4

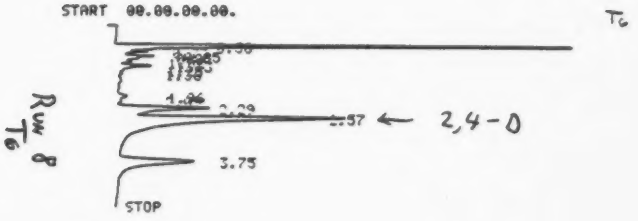
C-R1A
SMPL # 00
FILE # 8
REPT # 2144
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.59	37.3364		3839
0		0.73	0.296	T	70
0		0.9	1.6236	T	384
0		1.03	0.0895	TV	21
0		1.13	2.6272	T	622
0		1.49	0.3358	T	79
0		1.96	0.8283		196
0		2.11	0.2143	V	50
0		2.29	9.4037		2226
0		2.56	35.4986	V	8404
0		3.76	11.7481		2791
	TOTAL		99.9999		23675



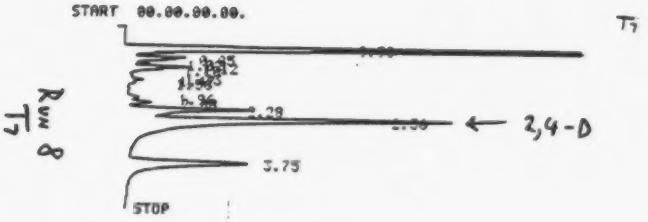
C-R1A
SMPL # 00
FILE # 8
REPT # 2145
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.59	35.5201		7397
0		0.66	9.1443	V	1904
0		0.73	1.3691	V	285
0		0.9	3.5181	V	732
0		1.02	0.5847	V	121
0		1.12	2.6285	V	547
0		1.36	0.5977	V	124
0		1.57	0.1427	V	29
0		1.96	0.6504		135
0		2.11	0.1241	V	25
0		2.29	7.8863		1642
0		2.57	28.4342	V	5921
0		3.76	9.3992		1957
	TOTAL		100		20825



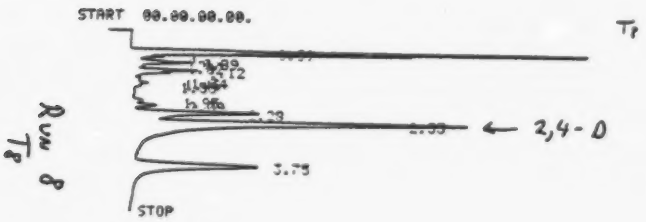
C-R1A
SMPL # 00
FILE # 8
REPT # 2146
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.58	41.584		6444
0		0.73	0.4875	T	73
0		0.85	0.8431	T	130
0		0.9	0.8429	TV	130
0		1.02	0.3729	TV	57
0		1.13	1.5695	T	243
0		1.25	0.129	TV	20
0		1.36	0.0941	TV	14
0		1.96	0.6652		103
0		2.09	0.2231	V	34
0		2.29	9.3864		1457
0		2.57	32.941	V	5114
0		3.75	10.9406		1698
	TOTAL		99.9999		15526



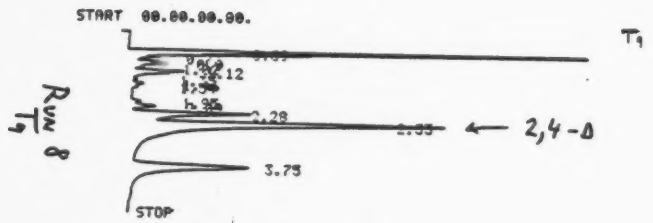
C-R1A
SMPL # 00
FILE # 8
REPT # 2147
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.58	43.7088		10993
0		0.85	3.0487	V	766
0		1.02	0.6033	V	151
0		1.12	2.0732	V	521
0		1.19	1.1969	V	301
0		1.53	0.3074	V	77
0		1.47	0.4188	V	105
0		1.56	0.2497	V	62
0		1.96	0.4674		117
0		2.08	0.855	V	215
0		2.28	7.9992	V	2012
0		2.56	28.4236	V	7150
0		3.75	10.6548		2680
	TOTAL		99.9999		25156



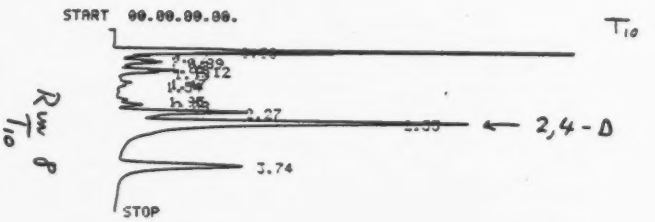
C-R1A
SMPL # 00
FILE # 8
REPT # 2148
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.59	37.4607		8224
0		0.77	0.2719	T	59
0		0.89	2.1764	T	477
0		1.02	0.1222	TV	26
0		1.12	3.2478	TV	713
0		1.34	0.2798	T	61
0		1.46	0.376	TV	82
0		1.55	0.2623	TV	57
0		1.95	0.4524		99
0		2.09	0.9967	V	218
0		2.28	9.0323	V	1982
0		2.55	32.7197	V	7183
0		3.75	12.6012		2766
	TOTAL		100		21954



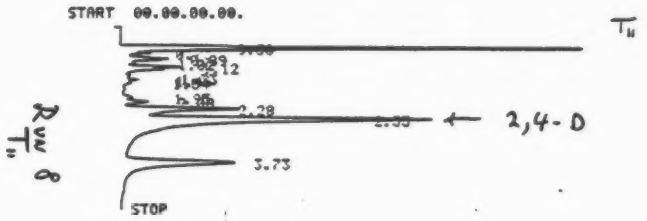
C-R1A
SMPL # 00
FILE # 8
REPT # 2149
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.59	36.1658		7255
0		0.73	0.2694	T	54
0		0.9	1.6983	T	340
0		1.02	0.1761	TV	35
0		1.12	2.9213	T	586
0		1.33	0.0739	TV	14
0		1.46	0.3587	TV	71
0		1.54	0.2409	TV	48
0		1.95	0.4877		97
0		2.09	1.1377	V	228
0		2.28	9.4714	V	1900
0		2.55	34.032	V	6827
0		3.75	12.9662		2601
	TOTAL		99.9999		20061



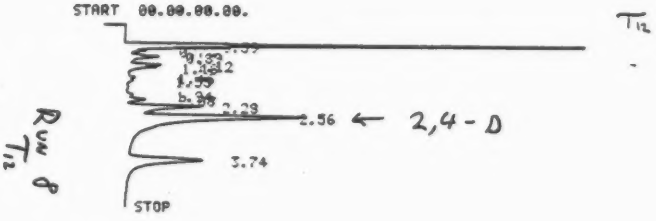
C-R1A
SMPL # 00
FILE # 8
REPT # 2151
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.58	35.0949		7577
0		0.72	0.3425	T	77
0		0.89	2.1189	T	457
0		1.02	0.1894	TV	40
0		1.12	2.0361	TV	439
0		1.18	1.1685	TV	252
0		1.47	0.5392	T	116
0		1.54	0.2513	TV	54
0		1.95	0.4399		94
0		2.08	1.0987	V	237
0		2.27	9.5635	V	2065
0		2.55	34.4151	V	7430
0		3.74	12.7393		2750
	TOTAL		100		21590



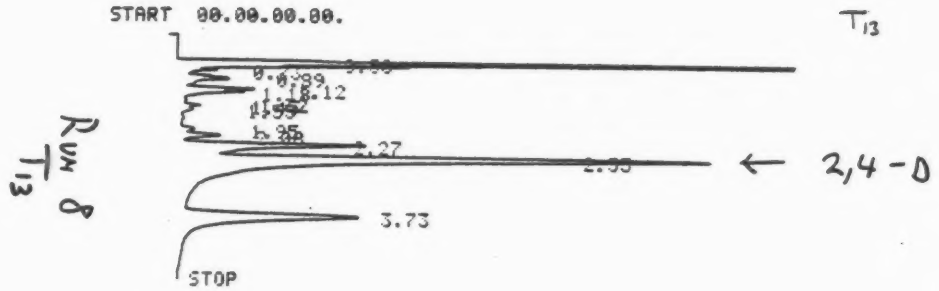
C-R1A
SMPL # 00
FILE # 8
REPT # 2152
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.58	35.4452		6986
0		0.73	0.2912	T	57
0		0.89	2.0129	T	396
0		1.02	0.1816	TV	35
0		1.12	3.376	TV	665
0		1.33	0.1912	TV	38
0		1.46	0.3881	TV	76
0		1.54	0.2845	TV	56
0		1.93	0.4559		89
0		2.08	1.197	V	233
0		2.28	9.4706	V	1866
0		2.55	34.2371	V	6747
0		3.73	12.4782		2459
	TOTAL		99.9999		19789



C-R1A
SMPL # 00
FILE # 8
REPT # 2153
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.59	38.6845		4996
0		0.73	0.2609	T	33
0		0.89	2.2678	T	292
0		1.12	1.8426	TV	238
0		1.18	1.4559	TV	188
0		1.46	0.4016	T	51
0		1.55	0.34	TV	43
0		1.94	0.4895		63
0		2.08	1.2641	V	163
0		2.28	9.1711	V	1184
0		2.56	30.805	V	3978
0		3.74	13.0163		1681
	TOTAL		99.9999		12916



C-R1A
SMPL # 00
FILE # 8
REPT # 2154
METHOD 41

#	NAME	TIME	CONC	MK	AREA
0		0.58	32.7588		7205
0		0.73	0.2159	T	47
0		0.89	1.7453	T	383
0		1.12	1.761	T	387
0		1.18	1.3666	TV	300
0		1.45	0.3221	TV	70
0		1.55	0.2815	TV	61
0		1.95	0.4761		104
0		2.08	1.2616	V	277
0		2.27	9.6447	V	2121
0		2.55	36.9811	V	8134
0		3.73	13.1847		2900
	TOTAL		99.9999		21995

APPENDIX C

GC/MS DATA

Primary objectives for the GC/MS analyses were to confirm that bromacil and 2,4-D had not significantly degraded from the time of receipt to the time of most recent experimentation, and to identify major constituents present in the two industrial samples.

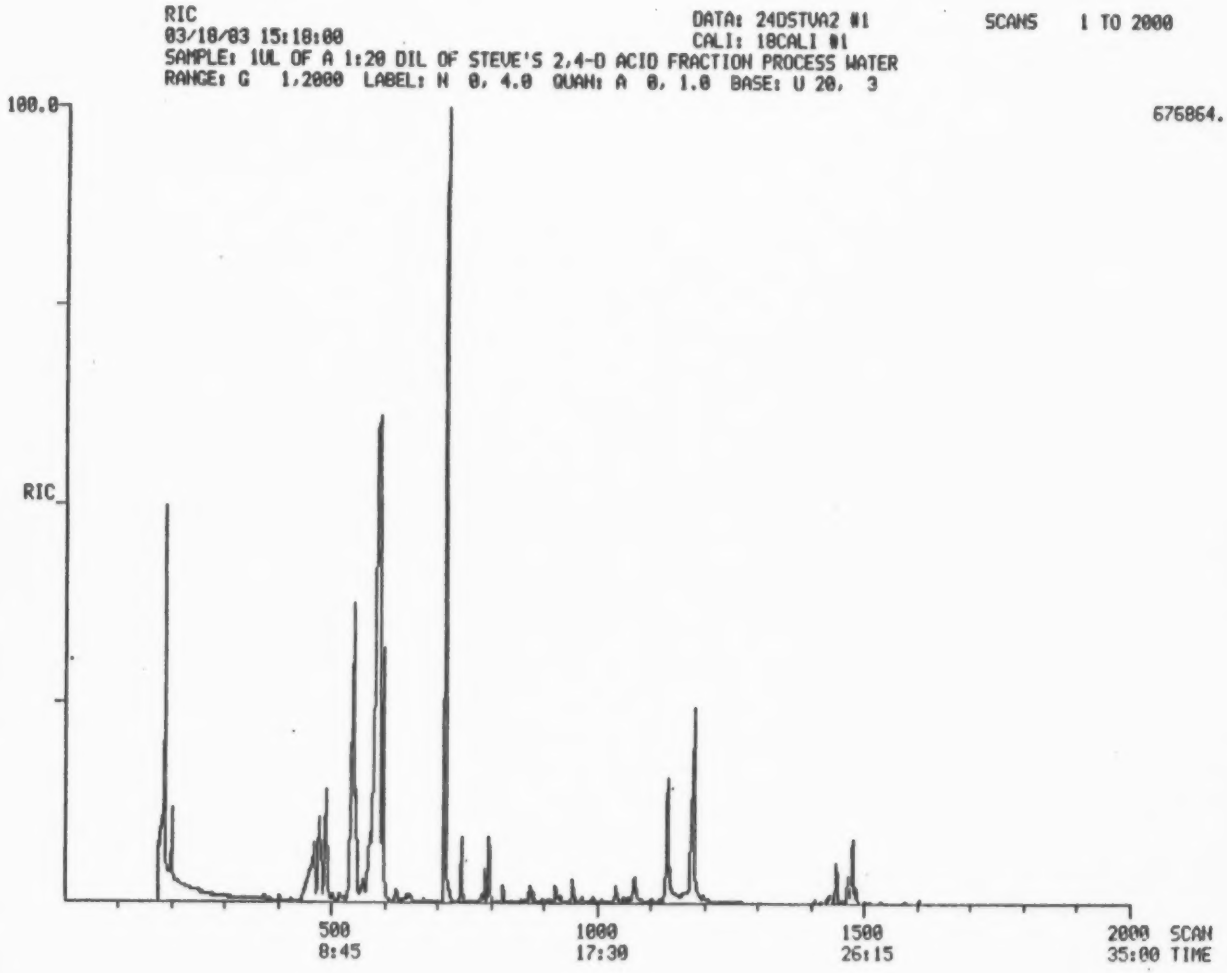
Analysis of the bromacil process water was conducted on the S-CUBED Finnigan 4021 GC/MS. A three percent OV-1, 6-ft column was used with 60/80 chromosorb as the packing material. The temperature program was set at 40°C isothermal for three minutes and then raised to 285°C at a rate of 6°C/min.

The bromacil process water did, in fact, contain bromacil, in addition to many other constituents. Other identified compounds include 2-isocyano butane, isobutyl methylester of carbamic acid, 1,2,3-thiadiozole, 3-methyl-2-cyclohexenone, 6-methyl-2-methoxy pyrazine, N,N-diethyl-1-propanamine, 2,2-dimethylpropylester of cyanic acid, and cyclohexanamine.

The 2,4-D process water was analyzed on the Finnigan 1020 GC/MS Data System quadrupole mass spectrometer with an electron multiplier detector. The column was a fused silica capillary 30-m x 0.25-mm narrow bore with SE54 liquid phase. The temperature program was set at 35° isothermal for 3 minutes and then raised to 285°C at a rate of 10°C/min.

Major components of the 2,4-D process water include aliphatic aldehydes (30.51 percent), chlorinated phenols (27.06 percent), aliphatic alcohols (16.03 percent) and olefins (4.0 percent).

Due to the GC/MS library limitations 2,4-D does not appear in the quantitation report, per se. Proof of its presence is found in the mass spectrum and mass chromatogram as noted in the following figures. Gas chromatograhy work performed on the run aliquots confirms this.



GC/MS Spectrum of 2,4-D Process Water

QUANTITATION REPORT FILE: OUTLIST

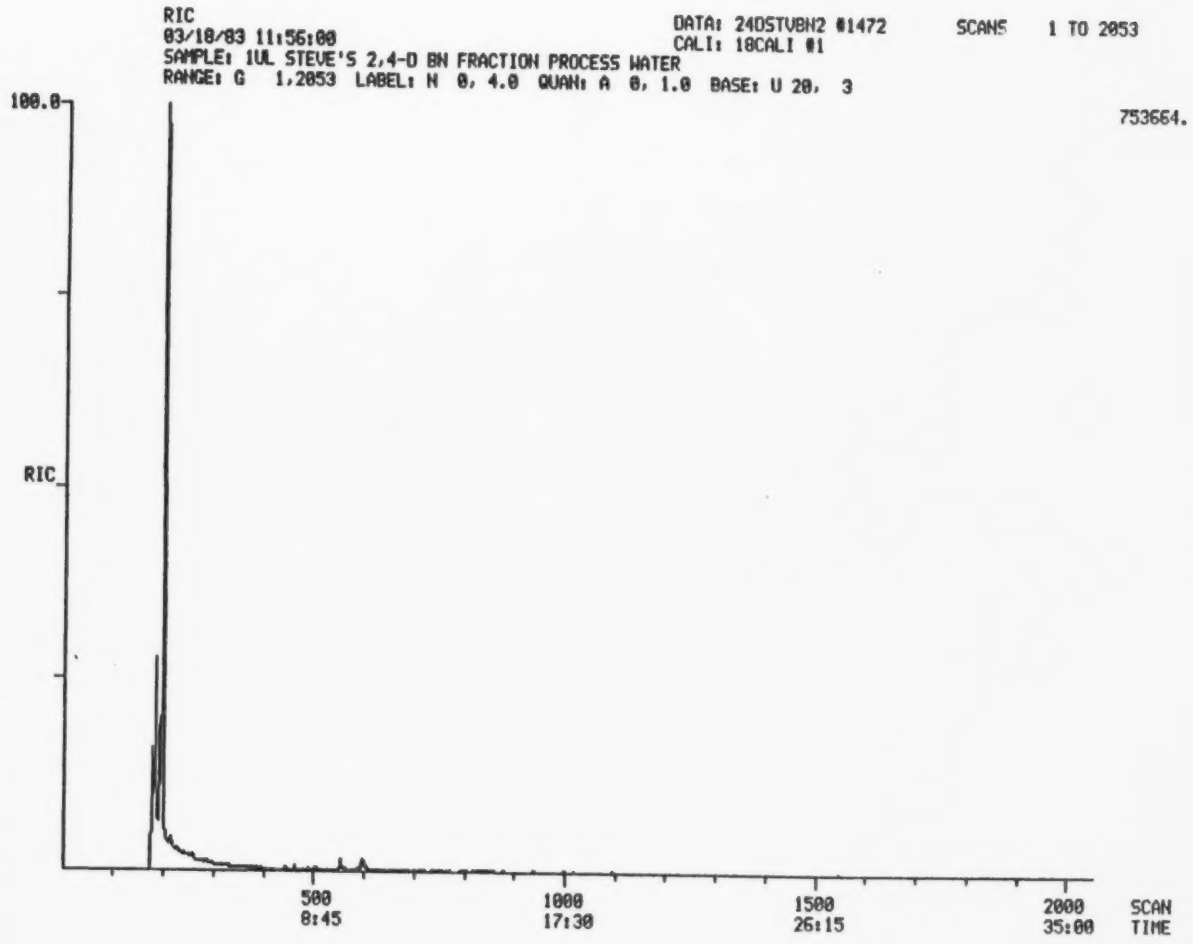
DATA: 24DSTVA2.TI
03/18/83 15:18:00
SAMPLE: 1UL OF A 1:20 DIL OF STEVE'S 2,4-D ACID FRACTION PROCESS WATER
CONDS.:
FORMULA: INSTR: OWA WT: 0.000
SUBMIT BY: LAB ANALYST: MDH ACCT. NO.:

AMOUNT=AREA(HGHT) * REF. AMNT/(REF. AREA(HGHT)* RESP. FACT)
RESP. FAC. FROM AVERAGE OF WHOLE RL

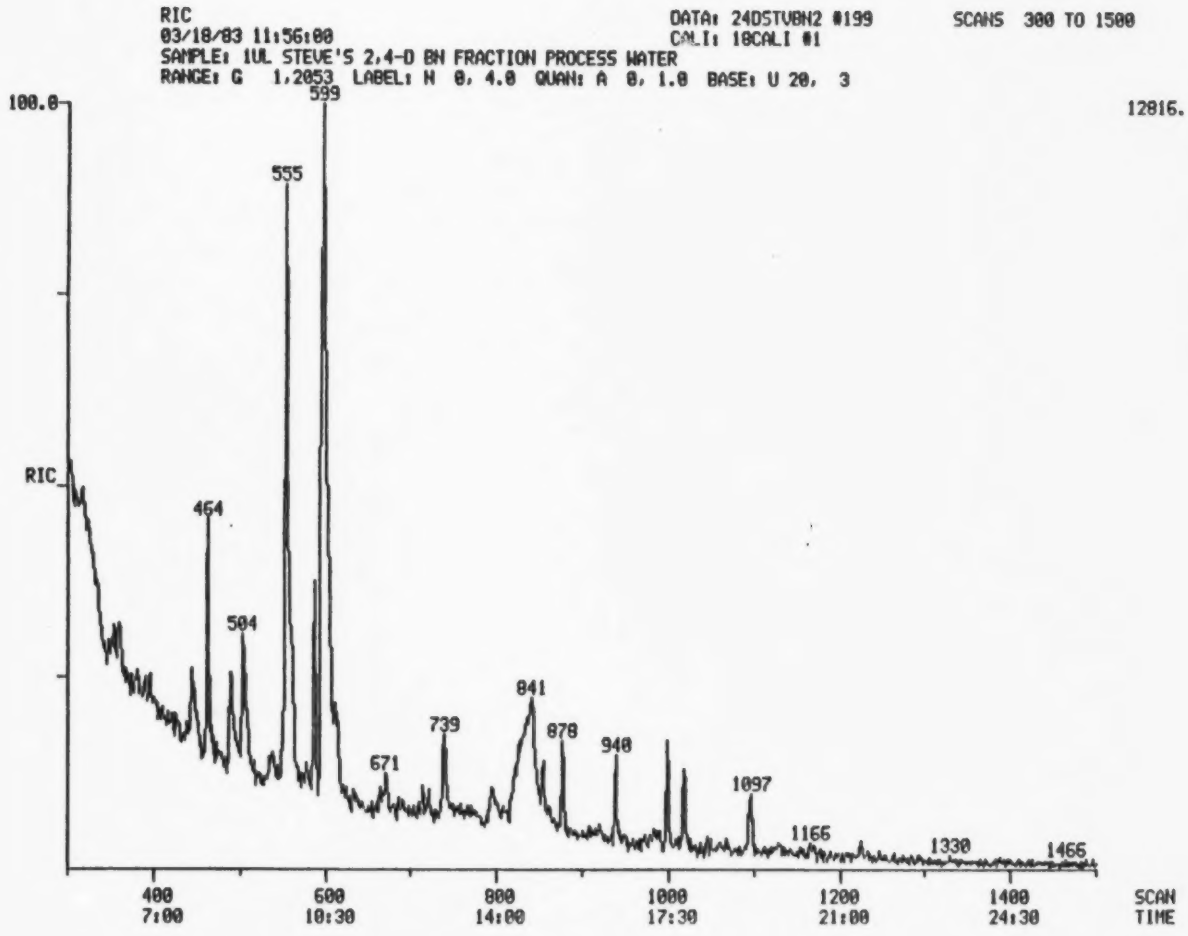
NO	NAME
1	BORANE, TRIFLUORO-
2	1-PROPANAMINE, 2-METHYL-N-(2-METHYLPROPYL)-
3	2-PYRROLIDINONE, 5-(CYCLOHEXYLMETHYL)-
4	CYCLOHEXENE
5	METHANE, DICHLORO-
6	1-HEXANOL
7	2(3H)-FURANONE, DIHYDRO-
8	1-HEXANOL, 5-METHYL-
9	1-PENTENE, 2, 3-DIMETHYL-
10	1-PROPENE, 2-METHYL-
11	1-HEXANOL, 5-METHYL-
12	ISOOCTANOL
13	1-DODECENE, 2-ETHYL-
14	2-PROPENAL
15	CYCLOPENTANE, 1-ETHYL-2-METHYL-, CIS-
16	CYCLOPROPANE, PENTYL-
17	1-HEXANOL, 3, 5, 5-TRIMETHYL-
18	1-HEXANOL, 5-METHYL-
19	PENTANE, 3-ETHYL-2, 4-DIMETHYL-
20	PHENOL, 2, 3-DICHLORO-
21	PHENOL, 2, 3-DICHLORO-
22	PHENOL, 2-BROMO-4-CHLORO-
23	PHENOL, 2-BROMO-4-CHLORO-
24	PHENOL, 2-BROMO-4-CHLORO-
25	ISOOCTANOL
26	1-OCTYNE
27	2(1H)-PYRIDINONE, 6-PHENYL-
28	PHENOL, 2, 4, 5-TRICHLORO-
29	MORPHOLINE, 3, 4-DIMETHYL-2-PHENYL-, (2R-TRANS)-
30	1H-BENZOTRIAZOLE
31	1H-INDOLE
32	ETHANE, 1, 1-DICHLORO-1-NITRO-
33	PROPANOYLCHLORIDE, 2, 2-DICHLORO-
34	4, 5-OCTADIEN-3-ONE, 2, 2, 7, 7-TETRAMETHYL-
35	PENTANE, 2, 2, 4-TRIMETHYL-4-NITRO-
36	1-OCTANOL, 3, 7-DIMETHYL-
37	PROPANE, 2-BROMO-1, 2-DICHLORO-
38	2-BUTENOICACID, BUTYLESTER
39	4-PENTENAL, 2-ETHYL-
40	ETHANE, 1, 1, 1-TRIETHOXY-
41	1, 3-PROPANEDIOL, 2, 2-BIS(HYDROXYMETHYL)-
42	PHENOL, 2, 3-DICHLORO-
43	DIAZENE, (4-METHYLPHENYL)PHENYL-, (Z)-
44	1-PENTANOL, 4-METHYL-2-PROPYL-
45	HEPTANE, 3, 3-DIMETHYL-
46	4, 5-OCTANEDIONE
47	1-PENTANOL, 2-ETHYL-4-METHYL-
48	1, 3-DIOXOLANE, 2, 2-DIETHYL-
49	ISOOCTANE, (ETHENYLOXY)-
50	4-OCTENOICACID, 6-ETHYL-3-HYDROXY-3, 7-DIMETHYL-, METHYLESTER
51	1-PENTANOL, 3-METHYL-2-PROPYL-
52	HEPTANE, 5-ETHYL-2-METHYL-
53	S-TETRAZINE, 3, 6-BIS(DIISOPROPYLAMINO)-
54	OCTANETHIOICACID, S-HEXYLESTER
55	1-NONENE, 4, 6, 8-TRIMETHYL-
56	5-NONANOL
57	1-NONENE, 4, 6, 8-TRIMETHYL-
58	PHENOL, 3, 5-DICHLORO-

NO	M/E	SCAN	TIME	REF	RRT	METH	AREA(HGHT)	AMOUNT	%TOT
1	RIC	176	3:05	14	0.298	A BV	193031.	4.027	1.20
2	RIC	182	3:11	14	0.308	A VV	296633.	6.189	1.84
3	RIC	189	3:18	14	0.320	A VV	909824.	18.982	5.64
4	RIC	202	3:32	14	0.342	A VB	165391.	3.451	1.03
5	RIC	251	4:24	14	0.425	A BB	15424.	0.322	0.10
6	RIC	402	7:02	14	0.680	A BB	8384.	0.175	0.05
7	RIC	469	8:12	14	0.794	A BB	460387.	9.605	2.85
8	RIC	478	8:22	14	0.809	A BV	415400.	8.667	2.58
9	RIC	491	8:36	14	0.831	A VB	396888.	8.281	2.46
10	RIC	503	8:48	14	0.851	A BB	15805.	0.330	0.10
11	RIC	516	9:02	14	0.873	A BB	29388.	0.613	0.18
12	RIC	544	9:31	14	0.920	A BB	1846770.	38.531	11.45
13	RIC	561	9:49	14	0.949	A BB	51152.	1.067	0.32
14	RIC	591	10:21	14	1.000	A BV	4792990.	100.000	29.72
15	RIC	598	10:28	14	1.012	A VB	473008.	9.869	2.93
16	RIC	623	10:54	14	1.054	A BB	38740.	0.808	0.24
17	RIC	643	11:15	14	1.088	A BV	40771.	0.851	0.25
18	RIC	649	11:21	14	1.098	A VB	18389.	0.384	0.11
19	RIC	675	11:49	14	1.142	A BB	5312.	0.111	0.03
20	RIC	716	12:32	14	1.212	A BB	2751520.	57.407	17.06
21	RIC	746	13:03	14	1.262	A BB	173138.	3.612	1.07
22	RIC	790	13:49	14	1.337	A BV	106487.	2.222	0.66
23	RIC	797	13:57	14	1.349	A VB	180606.	3.768	1.12
24	RIC	823	14:24	14	1.393	A BB	42145.	0.879	0.26
25	RIC	859	15:02	14	1.453	A BV	6718.	0.140	0.04
26	RIC	864	15:07	14	1.462	A VV	8220.	0.171	0.05
27	RIC	873	15:17	14	1.477	A VV	40768.	0.851	0.25
28	RIC	879	15:23	14	1.487	A VB	34800.	0.726	0.22
29	RIC	912	15:58	14	1.543	A BB	14444.	0.301	0.09
30	RIC	921	16:07	14	1.558	A BV	55209.	1.152	0.34
31	RIC	931	16:18	14	1.575	A VB	16451.	0.343	0.10
32	RIC	953	16:41	14	1.613	A BV	56319.	1.175	0.35
33	RIC	959	16:47	14	1.623	A VV	14938.	0.312	0.09
34	RIC	973	17:02	14	1.646	A VB	23754.	0.496	0.15
35	RIC	991	17:21	14	1.677	A BB	20810.	0.434	0.13
36	RIC	1035	18:07	14	1.751	A BB	48660.	1.015	0.30
37	RIC	1049	18:21	14	1.775	A BB	12070.	0.252	0.07
38	RIC	1059	18:32	14	1.792	A BV	8626.	0.180	0.05
39	RIC	1070	18:43	14	1.810	A VB	127999.	2.671	0.79
40	RIC	1132	19:49	14	1.915	A BB	493299.	10.292	3.06
41	RIC	1165	20:23	14	1.971	A BV	21118.	0.441	0.13
42	RIC	1183	20:42	14	2.002	A VB	1074680.	22.422	6.66
43	RIC	1199	20:59	14	2.029	A BB	9412.	0.196	0.06
44	RIC	1407	24:37	14	2.381	A BB	10115.	0.211	0.06
45	RIC	1430	25:01	14	2.420	A BV	13806.	0.288	0.09
46	RIC	1438	25:10	14	2.433	A VV	35320.	0.737	0.22
47	RIC	1449	25:21	14	2.452	A VV	121372.	2.532	0.75
48	RIC	1455	25:28	14	2.462	A VB	8088.	0.169	0.05
49	RIC	1471	25:45	14	2.489	A BV	90038.	1.879	0.56
50	RIC	1479	25:53	14	2.503	A VV	259638.	5.417	1.61
51	RIC	1485	25:59	14	2.513	A VB	40141.	0.837	0.25
52	RIC	1502	26:17	14	2.541	A BV	4031.	0.084	0.02
53	RIC	1511	26:27	14	2.557	A VB	4394.	0.092	0.03
54	RIC	1531	26:48	14	2.591	A BB	7486.	0.156	0.05
55	RIC	1577	27:36	14	2.668	A BB	5231.	0.109	0.03
56	RIC	1597	27:57	14	2.702	A BV	1842.	0.038	0.01
57	RIC	1604	28:04	14	2.714	A VV	10397.	0.217	0.06
58	RIC	1611	28:12	14	2.726	A VB	1753.	0.037	0.01

NAM NUM:	WT	FORMULA	NAME
NB 9680:	68	. B. F3	BORANE, TRIFLUORO-
NB 1298:	129	C8. H19. N	1-PROPANAMINE, 2-METHYL-N-(2-METHYLPROPYI
NB10772:	181	C11. H19. O. N	2-PYRROLIDINONE, 5-(CYCLOHEXYLMETHYL)-
NB 1289:	82	C6. H10	CYCLOHEXENE
NB 270:	84	C. H2. CL2	METHANE, DICHLORO-
NB 1312:	102	C6. H14. O	1-HEXANOL
NB 765:	86	C4. H6. O2	2(3H)-FURANONE, DIHYDRO-
NB 3593:	116	C7. H16. O	1-HEXANOL, 5-METHYL-
NB 7089:	98	C7. H14	1-PENTENE, 2, 3-DIMETHYL-
NB 1413:	56	C4. H8	1-PROPENE, 2-METHYL-
NB 3593:	116	C7. H16. O	1-HEXANOL, 5-METHYL-
NB15278:	130	C8. H18. O	ISOOCTANOL
NB12963:	196	C14. H28	1-DODECENE, 2-ETHYL-
NB 1102:	56	C3. H4. O	2-PROPENAL
NB 4379:	112	C8. H16	CYCLOPENTANE, 1-ETHYL-2-METHYL-, CIS-
NB 6430:	112	C8. H16	CYCLOPROPANE, PENTYL-
NB 7130:	144	C9. H20. O	1-HEXANOL, 3, 5, 5-TRIMETHYL-
NB 3593:	116	C7. H16. O	1-HEXANOL, 5-METHYL-
NB 4664:	128	C9. H20	PENTANE, 3-ETHYL-2, 4-DIMETHYL-
NB 2992:	162	C6. H4. O. CL2	PHENOL, 2, 3-DICHLORO-
NB 2992:	162	C6. H4. O. CL2	PHENOL, 2, 3-DICHLORO-
NB 3900:	206	C6. H4. O. CL. BR	PHENOL, 2-BROMO-4-CHLORO-
NB 3900:	206	C6. H4. O. CL. BR	PHENOL, 2-BROMO-4-CHLORO-
NB 3900:	206	C6. H4. O. CL. BR	PHENOL, 2-BROMO-4-CHLORO-
NB15278:	130	C8. H18. O	ISOOCTANOL
NB 3623:	110	C8. H14	1-OCTYNE
NB12680:	171	C11. H9. O. N	2(1H)-PYRIDINONE, 6-PHENYL-
NB 739:	196	C6. H3. O. CL3	PHENOL, 2, 4, 5-TRICHLORO-
NB 3680:	191	C12. H17. O. N	MORPHOLINE, 3, 4-DIMETHYL-2-PHENYL-, (2R-TI
NB 706:	119	C6. H5. N3	1H-BENZOTRIAZOLE
NB 1488:	117	C8. H7. N	1H-INDOLE
NB 3173:	143	C2. H3. O2. N. CL2	ETHANE, 1, 1-DICHLORO-1-NITRO-
NB15033:	160	C3? H3. O. CL3	PROPANOYLCHLORIDE, 2, 2-DICHLORO-
NB12820:	180	C12. H20. O	4, 5-OCTADIEN-3-ONE, 2, 2, 7, 7-TETRAMETHYL-
NB 8402:	159	C8. H17. O2. N	PENTANE, 2, 2, 4-TRIMETHYL-4-NITRO-
NB 1058:	158	C10. H22. O	1-OCTANOL, 3, 7-DIMETHYL-
NB12098:	190	C3. H5. CL2. BR	PROPANE, 2-BROMO-1, 2-DICHLORO-
NB 9492:	142	C8. H14. O2	2-BUTENOICACID, BUTYLESTER
NB 8321:	112	C7. H12. O	4-PENTENAL, 2-ETHYL-
NB 390:	162	C8. H18. O3	ETHANE, 1, 1, 1-TRIETHOXY-
NB 1427:	136	C5. H12. O4	1, 3-PROPANEDIOL, 2, 2-BIS(HYDROXYMETHYL)-
NB 2992:	162	C6. H4. O. CL2	PHENOL, 2, 3-DICHLORO-
NB 9147:	196	C13. H12. N2	DIAZENE, (4-METHYLPHENYL)PHENYL-, (Z)-
NB20533:	144	C9. H20. O	1-PENTANOL, 4-METHYL-2-PROPYL-
NB 7532:	128	C9. H20	HEPTANE, 3, 3-DIMETHYL-
NB 8488:	142	C8. H14. O2	4, 5-OCTANEDIONE
NB 1086:	130	C8. H18. O	1-PENTANOL, 2-ETHYL-4-METHYL-
NB 7764:	130	C7. H14. O2	1, 3-DIOXOLANE, 2, 2-DIETHYL-
NB18318:	156	C10. H20. O	ISOOCTANE, (ETHENYLOXY)-
NB19172:	228	C13. H24. O3	4-OCTENOICACID, 6-ETHYL-3-HYDROXY-3, 7-DI
NB20532:	144	C9. H20. O	1-PENTANOL, 3-METHYL-2-PROPYL-
NB10410:	142	C10. H22	HEPTANE, 5-ETHYL-2-METHYL-
NB12849:	280	C14. H28. N6	S-TETRAZINE, 3, 6-BIS(DIISOPROPYLAMINO)-
NB22621:	244	C14. H28. O. S	OCTANETHIOICACID, S-HEXYLESTER
NB20693:	168	C12. H24	1-NONENE, 4, 6, 8-TRIMETHYL-
NB 3493:	144	C9. H20. O	5-NONANOL
NB20693:	168	C12. H24	1-NONENE, 4, 6, 8-TRIMETHYL-
NB 3117:	162	C6. H4. O. CL2	PHENOL, 3, 5-DICHLORO-



GC/MS Spectrum of 2,4-D Process Water



GC/MS Spectrum of 2,4-D Process Water

QUANTITATION REPORT FILE: OUTLIST

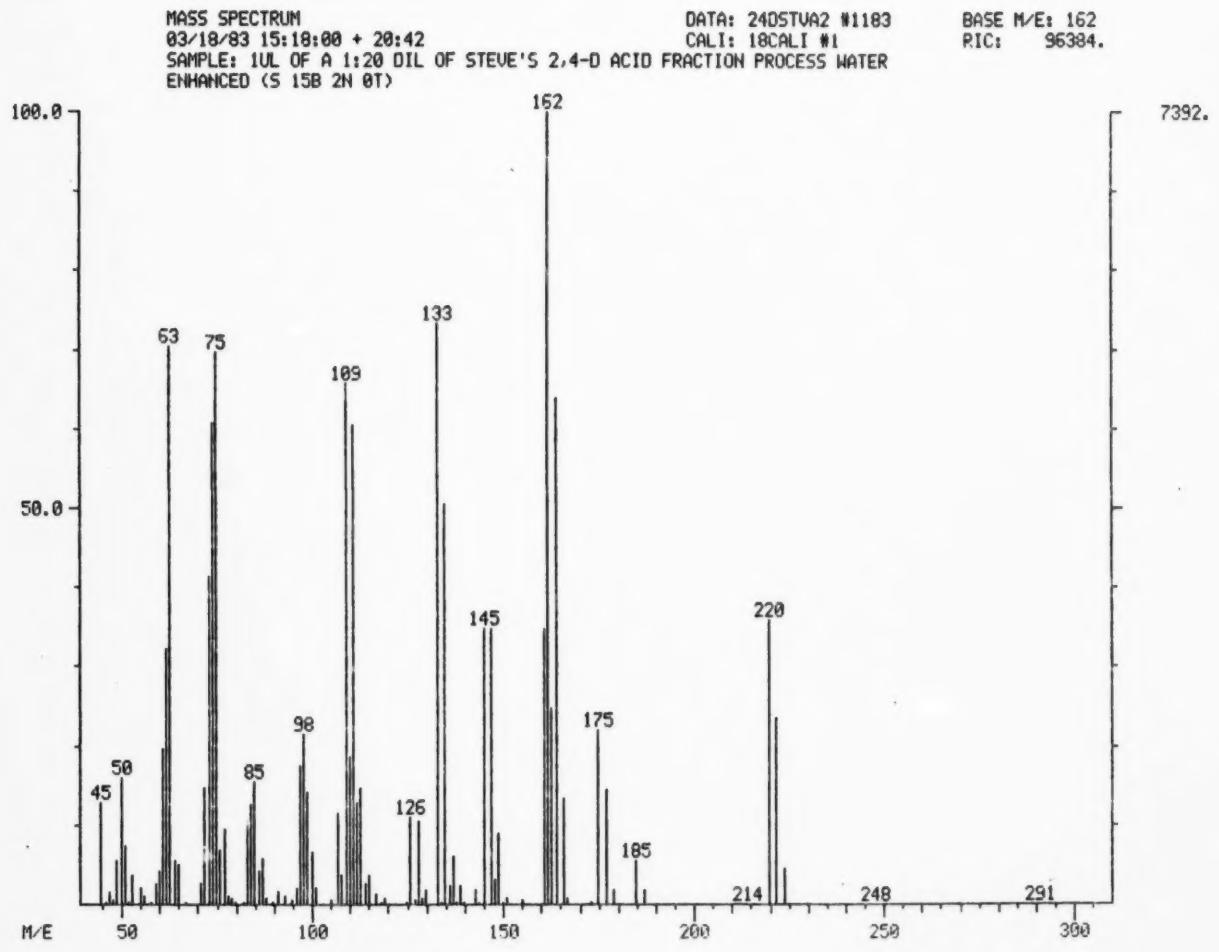
DATA: 24DSTVBN2.TI
03/18/83 11:56:00
SAMPLE: 1UL STEVE'S 2,4-D BN FRACTION PROCESS WATER
CONDS.:
FORMULA: INSTR: OWA WT: 0.000
SUBMIT BY: LAB ANALYST: MDH ACCT. NO.:

AMOUNT=AREA(HGHT) * REF. AMNT/(REF. AREA(HGHT)* RESP. FACT)
RESP. FAC. FROM AVERAGE OF WHOLE .RL

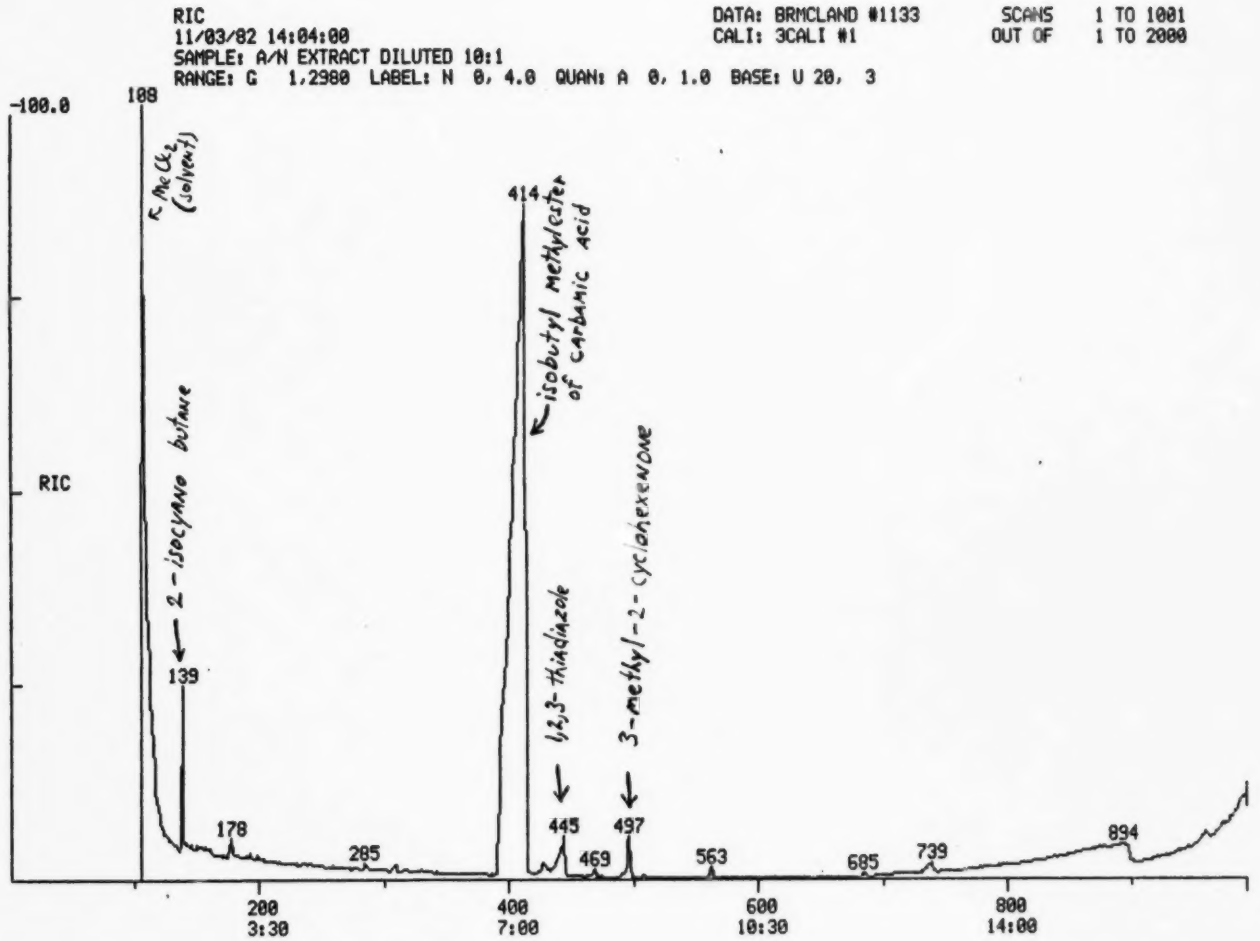
NO	NAME
1	METHANE, DICHLORO-
2	1-PENTENE, 2-METHYL-
3	1-BUTANOL
4	1,3-BUTADIENE, 2,3-DIMETHYL-
5	ETHENE, TRICHLORO-
6	ETHANAMINE, N-ETHYL-N-\(ETHYLTHIO)METHYL\-
7	2(3H)-FURANONE, DIHYDRO-
8	CYCLOPROPANE, BUTYL-
9	1-HEXANOL, 4-METHYL-
10	ISOOCTANOL
11	2-PENTENE, 4-METHYL-, (Z)-
12	1-HEXENE, 3, 4-DIMETHYL-
13	PYRROLIDINE, 2-HEXYL-1-METHYL-
14	D8-TOLUENE(SURROGATE)
15	OXIRANE, ETHENYL-
16	PHOSPHONICDIFLUORIDE
17	CYCLOBUTANECARBONITRILE, 3, 3-DIMETHYL-
18	2,2'-BI-1,3-DIOXOLANE
19	HEPTANE, 3, 5-DIMETHYL-
20	CYCLOPENTANE, 1, 1, 3-TRIMETHYL-

NO	M/E	SCAN	TIME	REF	RRT	METH	AREA(HGHT)	AMOUNT		%TOT
1	RIC	177	3:06	4	0.889	A BV	337408.	13.497		7.90
2	RIC	184	3:13	4	0.925	A VV	975296.	39.015		22.85
3	RIC	191	3:21	4	0.960	A VV	159872.	6.395		3.74
4	RIC	199	3:29	4	1.000	A VB	2499800.	100.000		58.55
5	RIC	215	3:46	4	1.080	A BB	23224.	0.929		0.54
6	RIC	257	4:30	4	1.291	A BB	42285.	1.692		0.99
7	RIC	464	8:07	4	2.332	A BB	9668.	0.387		0.23
8	RIC	490	8:34	4	2.462	A BB	6220.	0.249		0.15
9	RIC	504	8:49	4	2.533	A BB	10790.	0.432		0.25
10	RIC	555	9:43	4	2.789	A BB	50814.	2.033		1.19
11	RIC	588	10:17	4	2.955	A BB	10869.	0.435		0.25
12	RIC	599	10:29	4	3.010	A BV	82333.	3.294		1.93
13	RIC	612	10:43	4	3.075	A VB	8093.	0.324		0.19
14	RIC	739	12:56	4	3.714	A BB	6576.	0.286	UG/L	0.17
15	RIC	828	14:29	4	4.161	A BV	9344.	0.374		0.22
16	RIC	836	14:38	4	4.201	A VV	13151.	0.526		0.31
17	RIC	841	14:43	4	4.226	A VB	10421.	0.417		0.24
18	RIC	878	15:22	4	4.412	A BB	4000.	0.160		0.09
19	RIC	1019	17:50	4	5.121	A BB	4072.	0.163		0.10
20	RIC	1097	19:12	4	5.513	A BB	4351.	0.174		0.10

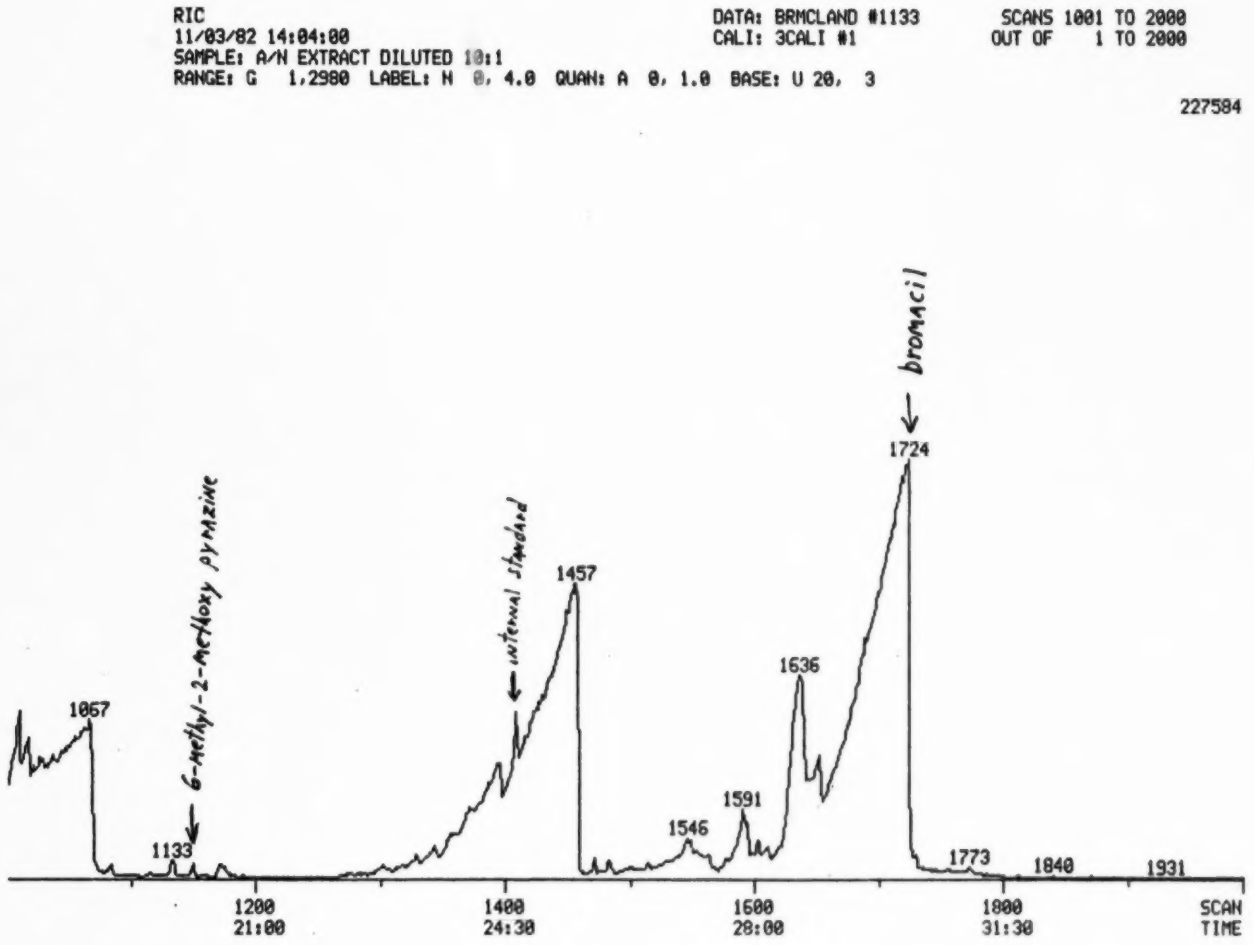
NAM NUM:	WT	FORMULA	NAME
NB 270:	84	C. H2. CL2	METHANE, DICHLORO-
NB 4011:	84	C6. H12	1-PENTENE, 2-METHYL-
NB 234:	74	C4. H10. O	1-BUTANOL
NB 2603:	82	C6. H10	1, 3-BUTADIENE, 2, 3-DIMETHYL-
NB 420:	130	C2. H. CL3	ETHENE, TRICHLORO-
NB 7157:	147	C7. H17. N. S	ETHANAMINE, N-ETHYL-N-\(ETHYLTHIO)METHYL
NB 765:	86	C4. H6. O2	2(3H)-FURANONE, DIHYDRO-
NB 4371:	98	C7. H14	CYCLOPROPANE, BUTYL-
NB 4142:	116	C7. H16. O	1-HEXANOL, 4-METHYL-
NB15278:	130	C8. H18. O	ISOOCTANOL
NB 3857:	84	C6. H12	2-PENTENE, 4-METHYL-, (Z)-
NB11651:	112	C8. H16	1-HEXENE, 3, 4-DIMETHYL-
NB 7123:	169	C11. H23. N	PYRROLIDINE, 2-HEXYL-1-METHYL-
NB25412:	100	C7. D8	D8-TOLUENE(SURROGATE)
NB 4362:	70	C4. H6. O	OXIRANE, ETHENYL-
NB10992:	86	H. O. F2. P	PHOSPHONICDIFLUORIDE
NB20442:	109	C7. H11. N	CYCLOBUTANECARBONITRILE, 3, 3-DIMETHYL-
NB 9138:	146	C6. H10. O4	2, 2'-BI-1, 3-DIOXOLANE
NB 4343:	128	C9. H20	HEPTANE, 3, 5-DIMETHYL-
NB 7883:	112	C8. H16	CYCLOPENTANE, 1, 1, 3-TRIMETHYL-



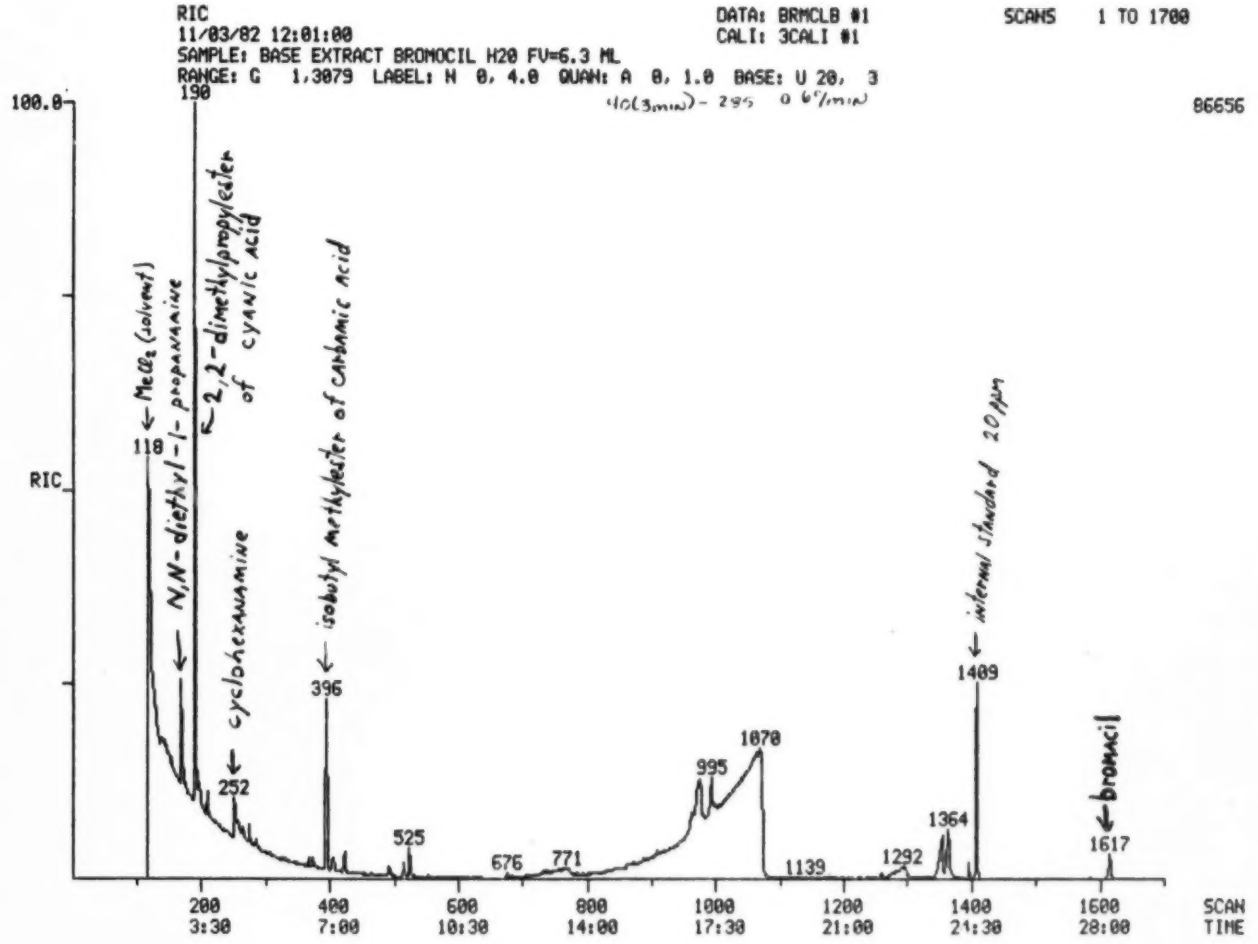
Mass Spectrum of 2,4-D Process Water Showing 2,4-D



GC/MS Spectrum of Bromacil Process Water



GC/MS Spectrum of Bromacil Process Water



GC/MS Spectrum of Bromacil Process Water

APPENDIX D

QUALITY ASSURANCE

Quality assurance work was conducted according to the approved Quality Assurance Project Plan. Each set of samples acquired was analyzed in conjunction with a replicate, spike, and laboratory blank. For the replicate, an additional 100 mL of the starting material ($S_{replicate}$) was analyzed. The "spike" sample consisted of an additional 100 mL of a run aliquot spiked with a known amount of the pesticide in question. The blank analysis was performed on 100 mL of distilled water, providing a means to expose laboratory or reagent contamination problems.

Quality assurance data were then derived from concentration values obtained for the replicates, spiked, and unspiked samples. Table D.1 displays the quality assurance results for Runs 2 through 8. Run 2 QA chromatograms and calibration standard chromatograms following Table D.1 are included as representative samples of quality assurance conducted for all eight project experiments.

A set of five to seven calibration standards were run on the GC with each series of analyses. This eliminated any problem with the variation in GC sensitivity and provided a calibration curve from which to determine concentration values for replicates, spiked and unspiked samples. Calibration curves were derived by performing a linear regression using the GC peak areas of the calibration standards.

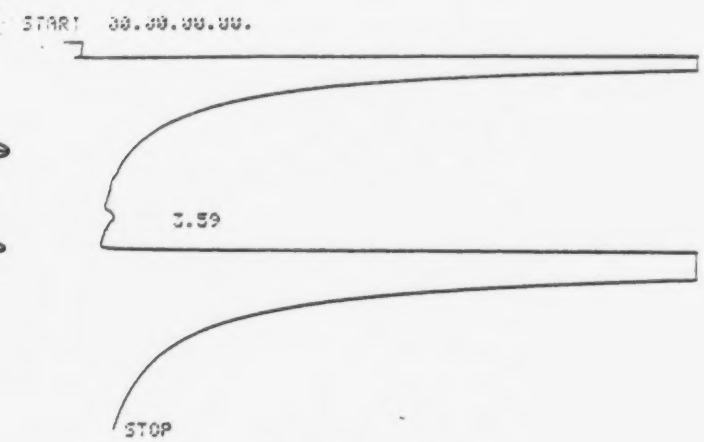
Calibration curves were also used to calculate pesticide concentrations for run aliquots. However, this was done only as a means to double-check efficiency values calculated from GC peak areas for the starting material (S) and aliquots(T_N). Efficiency values were calculated for Runs 2 through 8 to determine how parameter changes affect the RDC performance. This is not a quantitative analysis. It is a comparative analysis in which the ratio of T to S determines the efficiency.

Table D.1

QUALITY ASSURANCE RESULTS

Run No.	Percent Recovery	Mean Concentration of Replicate Measurements	Standard Deviation	Relative Standard Deviation	Accuracy	Completeness
2	80.0	430.7 ppm	1.8	0.6%	99.7%	100%
3	116.0	140.2 ppm	0.1	0.07%	100.7%	100%
4	67.8	151.7 ppm	3.2	2.9%	72.0%	100%
5	72.9	167.8 ppm	6.5	5.5%	78.0%	100%
6	68.0	64.4 ppm	7.5	16.6%	68.9%	100%
7	65.5	53.1 ppm	1.6	4.3%	67.5%	100%
8	86.2	56.2 ppm	2.7	6.8%	88.1%	100%

Run 2
Starting Material
S



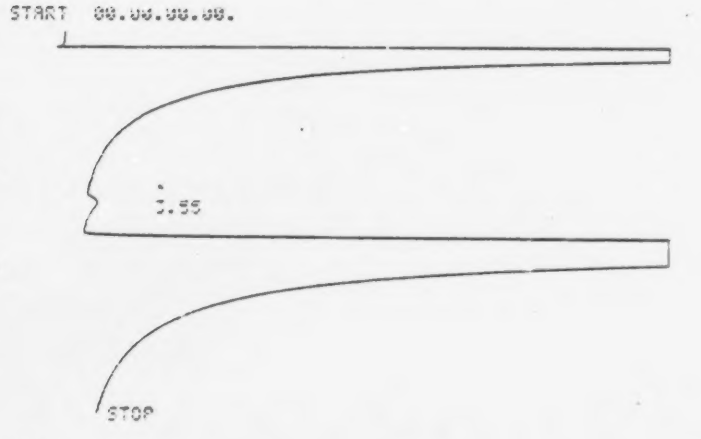
S

4.63 ← bromacil

C-RIH
SMPL # 00
FILE # 1
REPT # 2454
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		3.59	0.0000		222
		4.63			103137
	TOTAL		0.0000		103360

Run 2
Replicate Starting Material
S replicate

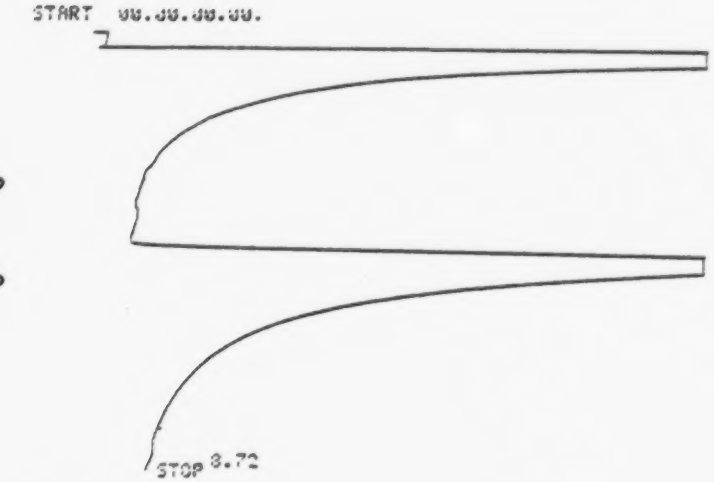


S Replicate

4.59 ← bromacil

C-RIH
SMPL # 00
FILE # 1
REPT # 2454
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		3.59	0.0000		330
		4.59			102462
	TOTAL		0.0000		102801



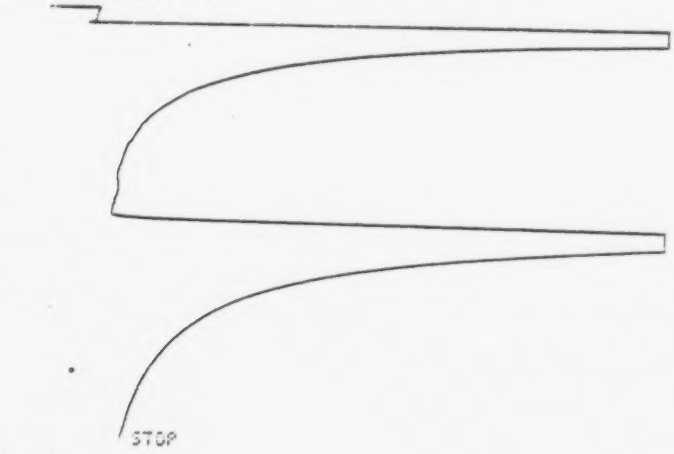
Run 2 T5

T5

4.68 ← bromacil

C-21A
SMPL # 00
FILE # 1
REPT # 2525
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.68	0.9139		71967
		8.72	0.0021	I	57
		TOTAL	0.921		72024



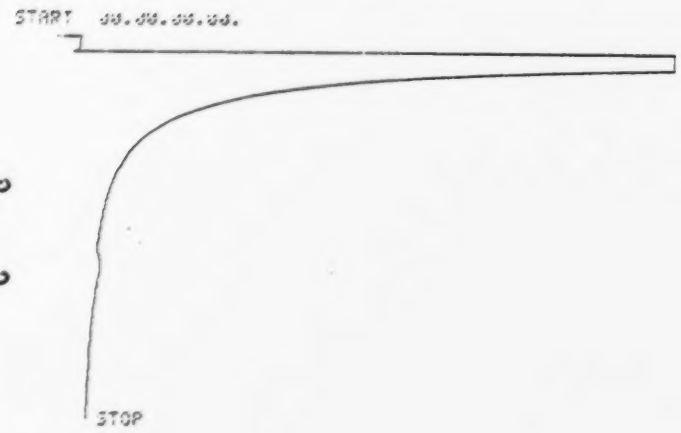
Run 2 T5 spike

T5 spike

4.69 ← bromacil

C-21A
SMPL # 00
FILE # 1
REPT # 2526
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.69	0.9913		72058
		TOTAL	0.9913		72058

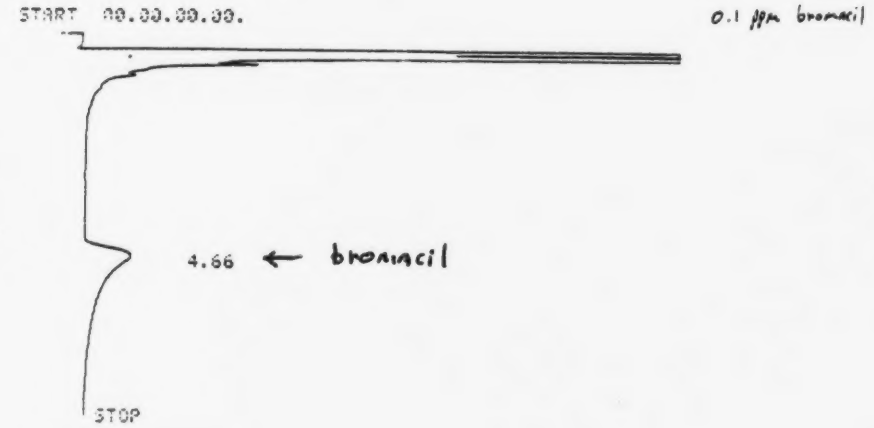


Run 2
Lab Blank

C-R1A
SMPL # 40
FILE # 1
REPT # 2426
METHOD 44

#	NAME	TIME	CONC	MK	AREA
	TOTAL		0		0

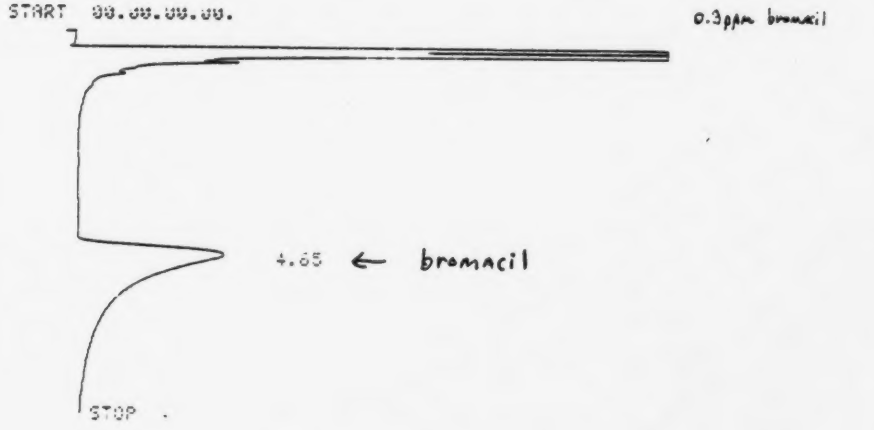
Run 2
0.1 ppm Calibration Standard



C-RIA
SMPL # 00.
FILE # 1
REPT # 2414
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.66			3266
	TOTAL		0		3266

Run 2
0.3 ppm Calibration Standard

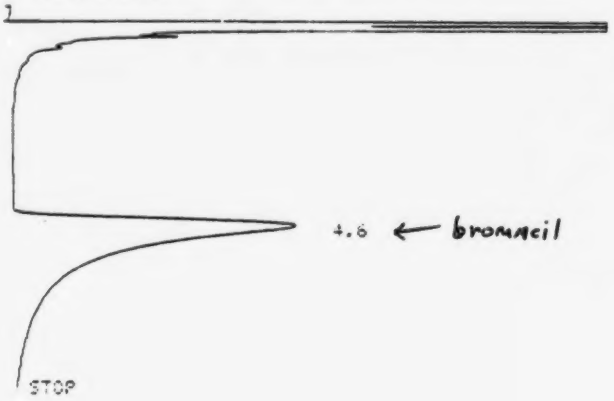


C-RIA
SMPL # 00
FILE # 1
REPT # 2415
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.65			12156
	TOTAL		0		12156

Run 2
0.5 ppm Calibration Standard

START 00.00.00.00. 0.5 ppm bromacil

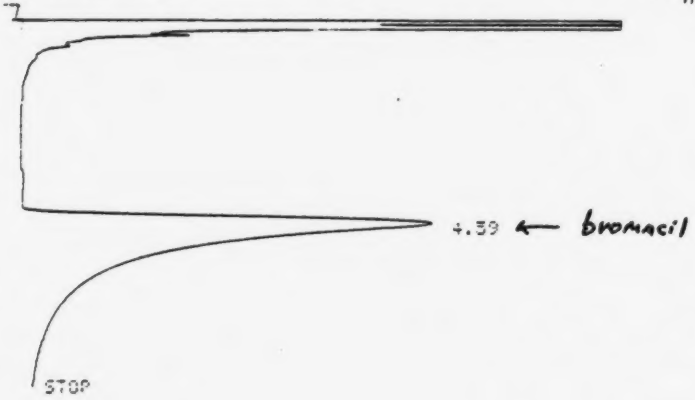


C-RUN .
SMPL # 00
FILE # 1
REPT # 2422
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.6			22043
	TOTAL		0		22043

Run 2
0.7 ppm Calibration Standard

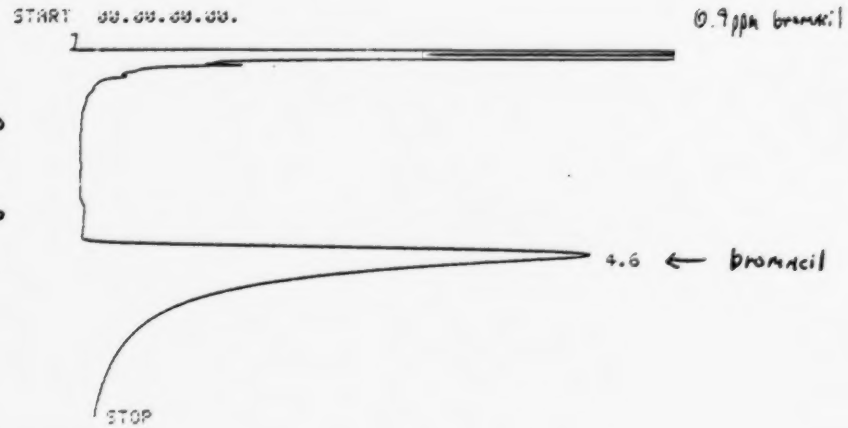
START 00.00.00.00. 0.7 ppm bromacil



C-RUN
SMPL # 00
FILE # 1
REPT # 2424
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.59			31863
	TOTAL		0		31863

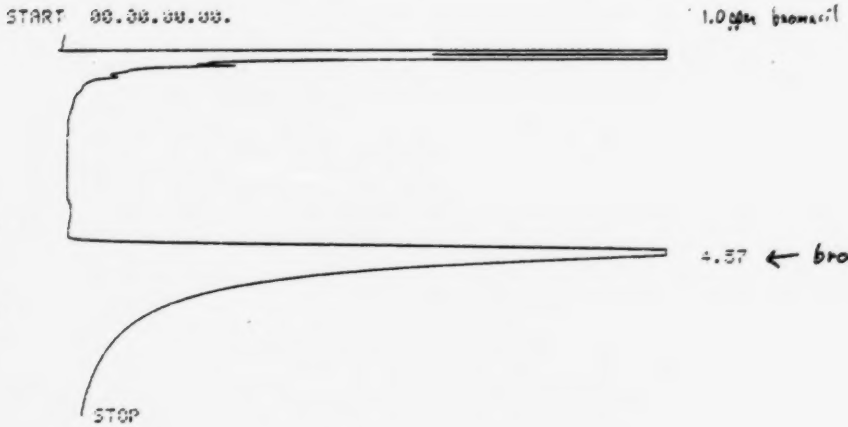
Run 2
0.9 ppm Calibration Standard



C-R1A
SMPL # 00
FILE # 1
REPT # 2400
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.6			40714
	TOTAL		0		40714

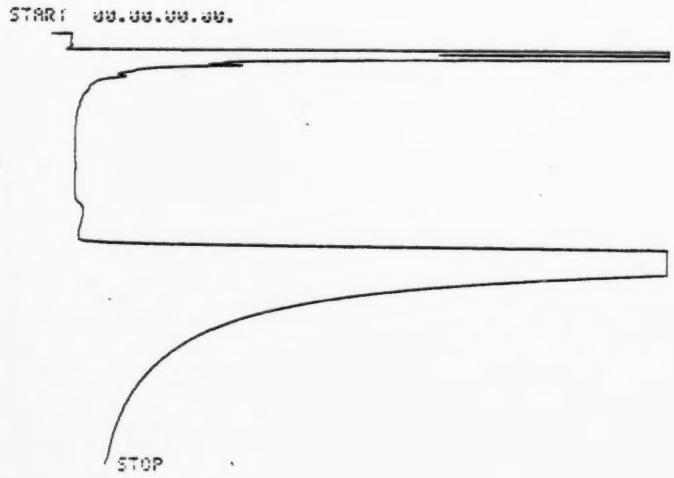
Run 2
1.0 ppm Calibration Standard



C-R1A
SMPL # 00
FILE # 1
REPT # 2402
METHOD 44

#	NAME	TIME	CONC	MK	AREA
		4.57			46763
	TOTAL		0		46763

Run 2
2.0 ppm Calibration Standard



CHAN		
SMPL #	00	
MULT #	1	
DILT #	1542	
METHOD	44	

#	NAME	TIME	CONC	MK	AREA
		4.65			95625
	TOTAL				95625